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## INSTRUMENTS FOR THE GRADUATION AND CALIBRATION OF VOLUMETRIC APPARATUS.

BY H. N. MORSE AND T. L. BLALOCK.

The apparatus represented in Fig. 1 is employed both for the graduation and the verification of liter and half-liter measuring-flasks. The delivering capacity of the bulb between the mark on the upper stem and the zero mark on the lower one must not exceed 500 cubic centimeters at the highest temperature at which the instrument is to be used; while the combined delivering capacity of the bulb and the graduated portion of the lower stem must not be less than half a liter at 0°. The lower stem is graduated in millimeter divisions which are numbered in both directions, in order that the instrument may be used in the inverted position if desired.

For the purpose of explaining the method of preparing an instrument of this kind for use, an account of an actual calibration will be given. The water delivered by the bulb, and also that delivered by the graduated portion of the stem, was weighed and its temperature noted. The delivering capacity of the bulb and of the stem was then calculated by the familiar formula,

$$V = P\frac{d}{p},$$

in which $P$ is the weight of the water when weighed in the air with brass weights (497.769 grams for the bulb and 3.0708 grams for the stem);

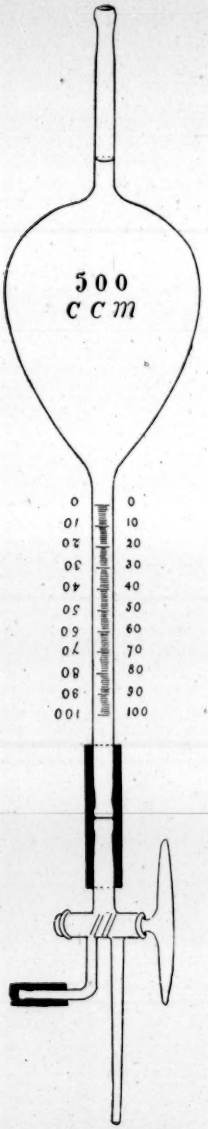


FIG. 1.

$p$ is the weight in a vacuum of one gram of water weighed in the air (1.001059 grams at ordinary temperatures); and

$d$ is the density of the water at the temperature of weighing (21.4°).

In this way the capacity of the bulb at 21.4° was found to be 499.324 cubic centimeters, and that of the stem, at the same temperature, 3.081 cubic centimeters.

The capacity of the bulb at 0°, 4°, 10°, 12.5°, 15°, 17.5°, 20°, 22.5°, 25°, 27.5° and 30°, was calculated by the formula,

$$V_1 = P\frac{p}{d}\{1+\gamma\,(t_1-t)\},\ \text{in which}$$

$P$, $p$ and $d$ have the same values as in the previous equation;

$\gamma$ is the expansion-coefficient of glass (0.000025);

$t_1$ is the temperature, 0°, 4° or 10°, etc., and

$t$ is the temperature of the water at the time of weighing.

The results of these calculations are given in the second column of the table which follows. No corresponding calculation was made for the stem, because the change in its capacity between 0° and 30° amounts to less than 0.0025 of a cubicentimeter. The inequalities of its bore were also found to be insignificant. Each millimeter division of the stem was therefore regarded as having a delivering capacity of 0.03081 cubicentimeter at all temperatures between 0° and 30°.

The next step was to find to what points on the graduated stem the water must be drawn in order to graduate a half-liter flask for each of the temperatures included in the first column. This was accomplished by dividing the differences between 500 and the several numbers in the second column by 0.03081. The results are given in the third column.

To prepare the instrument for use in the graduation and verification of apparatus when the so-called Mohr system is to be employed—*i. e.*, when the correction for air-displacement is to be dispensed with, the quantities in the second column were divided by the volumes at the different temperatures of one gram of water when weighed in the air with brass weights. These are:

| | |
|---|---|
| At 0°, 1.001185 ccm. | at 20°, 1.002812 ccm. |
| 4°, 1.001057 | 22.5°, 1.003363 |
| 10°, 1.001322 | 25°, 1.003974 |
| 12.5°, 1.001581 | 27.5°, 1.004651 |
| 15°, 1.001917 | 30°, 1.005380 |
| 17.5°, 1.002330 | |

The results are given in the fourth column of the table. The final step was to find to what point on the stem the water must be drawn in order to graduate flasks on the Mohr system for each of the temperatures recorded in the first column. For this purpose the capacity of the stem (3.081 cc.) was divided by 1.00233, the true volume of the Mohr unit at 17.5°, which gave 3.0738 as the capacity of the stem in Mohr units, or 0.030738 as the capacity of a single division. The differences between 500 and the several numbers in the fourth column were then divided by 0.030738, giving the numbers which are recorded in the fifth column. Strictly speaking, each difference should be divided by a different number; but the maximum error which could ever result from dividing all the differences by the volume of a gram of water when weighed in air at 17.5° (Mohr's standard temperature) is less than one hundredth of a cubicentimeter, and therefore inappreciable.

TABLE.

| Temperature. | Capacity of Bulb in cc. | Divisions of Stem to be added. | Capacity of ulb in Mohr units. | Divisions of Stem to be added. |
|---|---|---|---|---|
| 0° | 499.048 | 30.9 | 498.457 | 50.2 |
| 4° | 499.098 | 29.3 | 498.571 | 46.5 |
| 10° | 499.176 | 26.7 | 498.517 | 48.2 |
| 12.5° | 499.208 | 25.7 | 498.420 | 51.4 |
| 15° | 499.241 | 24.6 | 498.286 | 56.1 |
| 17.5° | 499.273 | 23.6 | 498.112 | 61.4 |
| 20° | 499.304 | 22.6 | 497.937 | 67.1 |
| 22.5° | 499.338 | 21.5 | 497.664 | 76.0 |
| 25° | 499.372 | 20.4 | 497.395 | 84.7 |
| 27.5° | 499.403 | 19.4 | 497.091 | 94.6 |
| 30° | 499.436 | 18.3 | 496.763 | 105.3 |

Capacity of one division of the stem in cubicentimeters, 0.03081.

Capacity of one division of the stem in Mohr units, 0.030738.

The use of the instrument is exceedingly simple. It is attached at the lower end to a Greiner and Friedrich's stop-cock, which is in turn connected by means of a rubber tube with a reservoir of distilled water placed somewhat higher than the instrument itself. The water should have about the temperature of the room. Its exact temperature, however, is a matter of indifference. Suppose now it is required to graduate a flask in such a way that it shall

have a capacity of 500 cubicentimeters at 20°. The whole apparatus is filled from the reservoir and emptied, once or twice, in order that the glass may acquire the temperature of the water. It is then again filled with water to the mark on the upper stem, and the water is delivered into the flask until the point indicated in the third column of the table (22.6) is reached. The flask is then placed upon a turn-table and marked with a diamond in the usual manner. If the flask is to be graduated for the same temperature on the Mohr system, the point to which the water must be drawn off (67.1) will be found on the same horizontal line in the fifth column. In the same way a flask may be graduated for any other temperature included in the table. The graduation will be correct for the given temperature whatever may be the temperature of the water at the time of graduation; since equal changes of temperature produce equal changes in the capacity of both the standard pipette and the flask. The instrument may be used equally well for the graduation of large gas-measuring apparatus.

Suppose, again, that it is required to find the capacity, at any given temperature, of a flask already graduated. The flask is filled to the mark from the pipette, and to the capacity of the bulb at the given temperature there is added the product of the reading on the stem and the volume of one millimeter division of the stem. If the capacity of the flask in cubicentimeters is to be found, the numbers in the second column will be employed for the bulb, and the value 0.03081 for the stem; while, if it is desired to find its capacity in Mohr units, the corresponding numbers in the fourth column will be used for the bulb, and 0.030738 for the stem divisions.

This method of graduation and verification has been found very satisfactory in practice. To determine what degree of accuracy may be expected from it, fourteen liter and half-liter flasks, representing the product of six different makers, were selected, and the capacity of each was determined both by means of the standard pipette and by weighing the water required to fill the flask. The maximum difference in the results obtained by the two methods was less than $\frac{1}{10000}$ of the capacity of the flask, while the average difference was $\frac{1}{25000}$. It is interesting, as showing to what extent the graduated apparatus of different makers may vary, to note that flasks of nominally equal capacity were in some cases found to differ by one-tenth of one per cent.

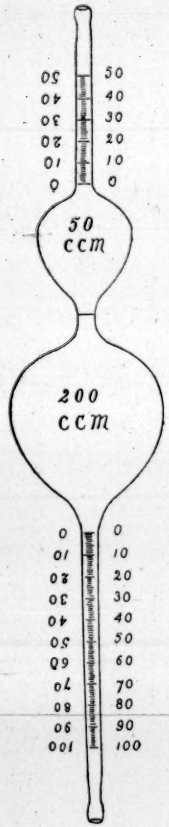


FIG. 2.

The interior of the pipette must, of course, be scrupulously cleansed.

The apparatus represented in Fig. 2 is used for the graduation and verification of smaller measuring-flasks. The capacities of the bulbs and of the stems are subject to the same limitations as in the preceding case; that is, the delivering capacity of the smaller bulb must not exceed 50, and that of the larger one 200 cubicentimeters, at the highest temperature at which the instrument is to be used, while the combined capacity of each bulb and its stem must not be less than 50 and 200 cubicentimeters respectively at 0°. The delivering capacity of each bulb and stem, at different temperatures, is determined, and the results are tabulated in the manner previously explained. 50-, 200-, or 250-cubicentimeter flasks can be graduated or their capacities determined by a single filling of the pipette. To graduate a 100-cubicentimeter flask the smaller bulb must be twice filled. The stop-cock may, of course, be attached to either end of the instrument.

Fig. 3 represents a modification of Ostwald's calibration pipette for burettes.[1] It differs from the original form in that a Greiner and Friedrich's stop-cock has been substituted for the side tube and pinch-cocks of the Ostwald apparatus. The advantage of such a substitution lies in the fact that it does away with the only objection to the original pipette, viz., the danger that the compression of the rubber connecting-tubes by the pinch-cocks may not always have the same effect upon the capacity of the ungraduated portion of the apparatus, *i. e.*, that portion of it which lies between the graduation of the burette and of the pipette. Another advantage of the

[1] Ztschr. anal. Chem. **22**, 549.

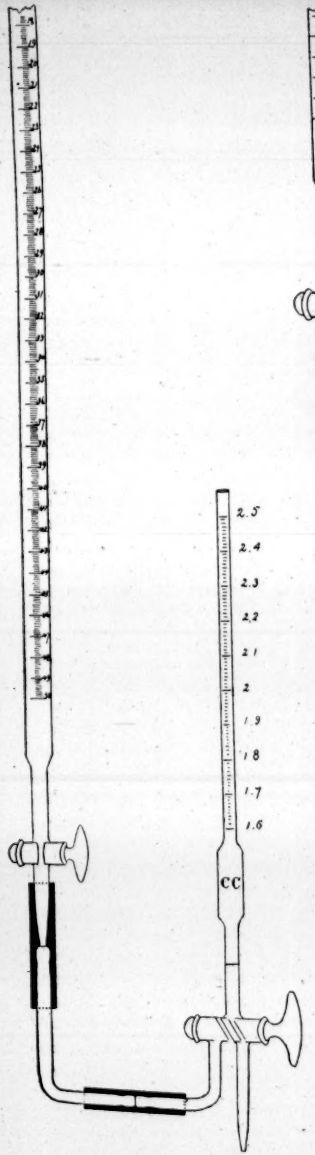
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
cc

FIG. 3.

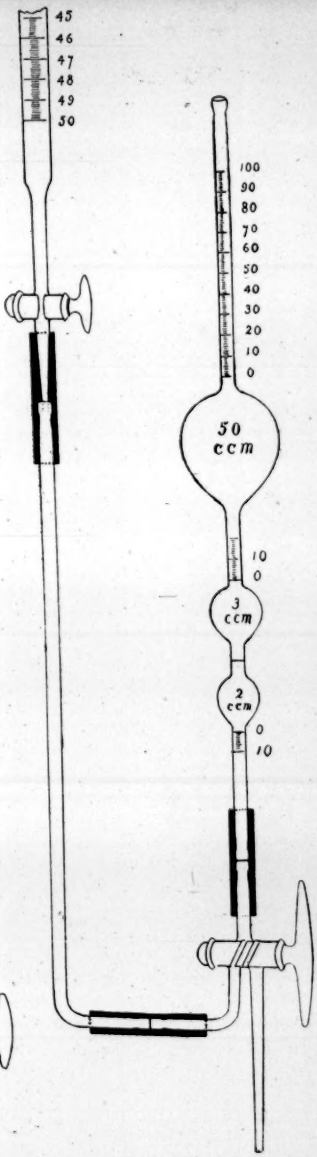
45
46
47
48
49
50
100
90
80
70
60
50
40
30
20
10
0
50 ccm
10
0
3 ccm
2 ccm
0
10

FIG. 4.

modified form is that mercury, as well as water, may be employed for the calibration of burettes. If mercury is used, the walls of the rubber connecting-tubes should be supported by winding them with cord or copper wire.

A still better form of calibrating pipette is shown in Fig. 4. The largest bulb, together with the graduated upper stem, is employed to determine the total delivering capacity of a burette at any temperature, while the smaller ones are used to ascertain the inequalities of its caliber. The largest bulb delivers somewhat less than 50 cubicentimeters at 30°, while the bulb and the upper graduated stem together deliver more than 50 cubicentimeters at 0°. The smaller bulbs and the graduated portions of the stem which belong to them are subject to the same relative limitations in respect to delivering capacity. In other words, at 30° the bulb marked 3 ccm. delivers a little less than 3, and that marked 2 ccm. a little less than 2 cubicentimeters, while the first together with the graduated portion of the stem above it, and the second with the graduated stem below it, will deliver not less than 3 and 2 cubicentimeters respectively at 0°. The delivering capacity of each bulb and of each graduated section of the stem is determined for all required temperatures, and the results are tabulated in the manner already described.

The procedure with a burette is as follows: The burette and the pipette are both filled with water to the upper limits of their graduation. It is convenient for the purpose of filling to insert between the burette and pipette a T-tube, one branch of which is supplied with a ground-glass stop-cock, and to connect this by means of a rubber tube with a supply of water which is placed somewhat above the upper limit of the graduation on the burette. Having filled both instruments, the water in the pipette is drawn down to the beginning of the graduation under the large bulb. The water in the burette is then allowed to flow into the pipette until the graduated portion of the former is emptied. The delivering capacity of the whole burette, at any temperature, may then be ascertained by reference to the table.

The method employed by us in correcting for the inequalities of caliber does not require the exact capacity of the smaller bulbs to be known. Equal quantities of water—approximately 2, 3 or 5 cubicentimeters—are drawn off, and a record is made of the successive readings upon the burette. The subsequent procedure will be better explained by an example. A burette which had

been graduated on the Mohr system for 15°, but which was to be used for solutions prepared at 20°, was found to have at the latter temperature a delivering capacity of 50.258 cubicentimeters. The burette was filled, and the water drawn off in quantities which exactly filled the smallest bulb of the pipette. The readings upon the burette corresponding to the successive pipettefuls are given in the table under R. The 25th and last reading was 49.52. The capacity of the burette to this point on its graduation was found by the proportion 50 : 50.258 : 49.52 : $x$, to be 49.7755 cubicentimeters. The volume of a bulbful was, therefore, $\frac{49.7755}{25}$, or 1.99102 cubicentimeters. The correct reading corresponding to each actual reading was then found by multiplying 1.99102 by the series of numbers from 1 to 25. The results are given under C. R. The differences, *i. e.*, the quantities to be added as corrections to the actual readings, are given under D. Finally, a curve of corrections for the burette was plotted upon cross-ruled paper, using a line representing the graduation upon the burette as the axis of abscissas, and the corrections under D as the ordinates.

| | R. | C. R. | D. |
|---|---|---|---|
| 1 | 1.95 | 1.99 | + 0.03 |
| 2 | 3.94 | 3.98 | + 0.04 |
| 3 | 5.93 | 5.97 | + 0.04 |
| 4 | 7.94 | 7.96 | + 0.02 |
| 5 | 9.91 | 9.96 | + 0.05 |
| 6 | 11.90 | 11.95 | + 0.05 |
| 7 | 13.85 | 13.94 | + 0 09 |
| 8 | 15.84 | 15.93 | + 0.09 |
| 9 | 17.83 | 17.92 | + 0.09 |
| 10 | 19.78 | 19.91 | + 0.13 |
| 11 | 21.74 | 21.90 | + 0.16 |
| 12 | 23.75 | 23.89 | + 0.14 |
| 13 | 25.74 | 25.88 | + 0.14 |
| 14 | 27.70 | 27.87 | + 0.17 |
| 15 | 29.70 | 29.87 | + 0.17 |
| 16 | 31.68 | 31.86 | + 0.18 |
| 17 | 33.65 | 33.85 | + 0.20 |
| 18 | 35.62 | 35.84 | + 0.22 |
| 19 | 37.60 | 37.83 | + 0.23 |
| 20 | 39.59 | 39.82 | + 0.23 |
| 21 | 41.58 | 41.81 | + 0.23 |
| 22 | 43.56 | 43.80 | + 0.24 |
| 23 | 45.55 | 45.79 | + 0.24 |
| 24 | 47.54 | 47.78 | + 0.24 |
| 25 | 49.52 | 49.78 | + 0.26 |
| | 50.00 | 50.26 | + 0.26 |

It will be readily seen that the table belonging to the pipette is so constructed that a curve of corrections for any other temperature, or for the Mohr system, can be drawn with equal facility.

*Note.* The apparatus here described was made by Mr. Emil Greiner of New York.

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Contribution from the Chemical Laboratory of the Costa Rican Government.

## NOTE ON THE INFLUENCE OF CERTAIN METALS ON THE STABILITY OF THE AMALGAM OF AMMONIUM.

By Gustave Michaud.

The metallic radicle ammonium, which cannot be obtained in a state of purity, seems to acquire some stability in the state of alloy with mercury. Other metals than mercury might possibly form alloys still more stable with the ammonium, and with a view to testing this I prepared a series of amalgams, each of which contained, besides mercury and ammonium, one of the metals given in the list below.

These amalgams were made by pouring 100 cc. of a solution of ammonium chloride, saturated at 25°, on a mixture of 5 cc. of sodium amalgam with 5 cc. of an amalgam of each metal. This latter amalgam, in turn, was obtained by placing sodium amalgam in contact with a salt of the metal. As a result of the method used for its preparation, the amount of the metal whose action was to be examined was proportional to the chemical equivalent of this metal. The sodium amalgam used was the same throughout all the experiments and contained 0.85 per cent. of sodium. The experiments were made simultaneously in graduated cylinders of 200 cc., in order to allow the measuring of the volume of the amalgam at any time. One of the graduated cylinders contained nothing but the sodium amalgam, to which 5 cc. of pure mercury had been added in order to have the same percentage of sodium as in the other cylinders.

From the beginning of the experiment two facts were plainly perceived, viz., that the volume of the amalgam of ammonium,

when made in the presence of a third metal, was in nearly every case less than that of the same amalgam when pure, and that, in some cases, there was no increase of volume at all, the ammonium being decomposed, in proportion as it was formed, into a mixture of ammonia and hydrogen, which escaped with a considerable effervescence.

The following table shows these facts and the relative influence of the principal metals on the stability of the amalgam of ammonium.

| Metal added to the amalgam of ammonium. | Increase of volume after addition of 100 cc. of a solution of chloride of ammonium. | Metal added to the amalgam of ammonium. | Increase of volume after addition of 100 cc. of a solution of chloride of ammonium. |
|---|---|---|---|
| None | 115 cc. | Fe | 110 cc. |
| Ag | 50 " | Mg | 115 " |
| Al | 115 " | Mn | 110 " |
| Au | 35 " | Pb | 65 " |
| Bi | 5 " | Pt | 0 " |
| Cd | 80 " | Sb | 30 " |
| Co | 30 " | Sn | 25 " |
| Cu | 105 " | Zn | 110 " |

It is impossible not to recognize a certain relation between the electric polarity of metals and the influence which they have on the stability of the amalgam of ammonium, the less electropositive metals being as a rule those which prevent the formation of the radicle. On the other hand this rule shows several exceptions. Aluminium and magnesium do not seem to have any influence whatever on the stability of ammonium amalgam, but they would probably interfere with it if it were possible to introduce them in large quantities in a liquid amalgam. At least an experiment in which I tried without result to prepare the amalgam with alum of aluminium and ammonium instead of ammonium chloride, led me to that conclusion, as it was evident that the presence of aluminium was the only factor that could prevent the formation of the ammonium.

To sum up the results of this investigation I may deduce the following conclusions:

1. When the radicle ammonium is set free in presence of an alloy of mercury and of one of the aforesaid metals, its stability is inferior to what it would be when associated with mercury alone.

2. A very small percentage of platinum in the amalgam of ammonium absolutely prevents the formation of the ammonium.

3. The power of decreasing the stability of the radicle ammonium is greater in the electro-negative metals, but is not proportional to their polarity.

4. In spite of the contrary conclusion of several chemists,[1] the amalgam of ammonium does contain the ammonium, for whenever a simple mixture of hydrogen and ammonia is evolved during the experiment, it has not the power to dilate the mercury and to give it the characteristic appearance of the amalgam of ammonium.

## MIXED DOUBLE HALIDES OF ANTIMONY AND POTASSIUM.

By Charles H. Herty.

Hoping to obtain evidence bearing upon the question of the constitution of double halides, R. W. Atkinson[2] took the plausible position that if the theory of molecular combination be true, as regards the formation of these compounds, then by mixing one equivalent of antimony trichloride with three of potassium bromide, and one of antimony tribromide with three of potassium chloride, two distinct isomeric salts of the general formula $K_3SbCl_3Br_3$ should be obtained, namely, $SbCl_3.3KBr$ and $SbBr_3.3KCl$. But on mixing the antimony and potassium salts in these proportions he obtained the same product in each case. This was confirmed by analysis of the compounds and by measurement of the crystals. From the analytical results he deduced the formula $SbCl_3Br_3K_3.1\frac{1}{2}H_2O$.

Atkinson found further evidence that no molecular combination had taken place in the fact that, on heating the above compound, fumes of antimony salts escaped, and a residue remained consisting of equivalent parts of potassium chloride and potassium bromide. From this fact he concludes that "This . . . also answers sufficiently the objection, that by the act of solution a redistribution of elements takes place, and that therefore we must obtain the same compound from whichever pairs we start. Grant-

[1] Landolt: Ztschr. Chem. [2], 5, 429. [2] J. Chem. Soc. 1883, 289.

ing that it were so, the crystals resulting would have one or other of the two constitutions $SbBr_3.3KCl$ or $SbCl_3.3KBr$, and on heating either all the bromine or all the chlorine would be driven off, not one-half of each."

By using varying proportions of antimony and potassium salts he obtained compounds to which he ascribed the formulas $Sb_2Cl_6Br_2K_2.2H_2O$ and $SbCl_3BrK.H_2O$.

In a recent article[1] I have shown that double halides of lead and potassium containing more than one halogen are not true salts, but isomorphous mixtures of double halides containing only one halogen. It has seemed advisable, therefore, to study these salts of Atkinson more carefully and determine whether they are true chemical compounds or isomorphous mixtures.

### *Preparation of Compounds.*

If it be true that definite chemical compounds are formed by the union of an alkali halide with the halide of a heavy metal, the halogen being different in the two substances, then by varying the proportion of one or the other of these substances we should expect the same salt to be formed under at least slight variations of conditions. In the case of mixed double halides of lead and potassium it has been shown that, by using the same quantities of potassium bromide, but slightly varying quantities of lead iodide, compounds could be obtained, each of which showed a slight variation in composition from that of any of the other compounds.

Again, by substituting for portions of potassium bromide equivalent quantities of potassium iodide, and for lead iodide equivalent quantities of lead bromide, compounds could be obtained at will, in accordance with the variations in the composition of the solutions from which they were formed.

In the following investigation the latter method has been adopted for determining the character of the compounds. In this manner all of the solutions contained the same weights of antimony and potassium, but varying weights of bromine and chlorine. 60 cc. of water, heated almost to boiling, was used in the preparation of each solution. Beginning with the proportions indicated by the formula $SbCl_3.3KBr$, and using in each case the same quantity of antimony chloride, a series of solutions was prepared by substituting for varying quantities of potassium bromide equiv-

[1] This Journal **15**, 81.

alent quantities of potassium chloride. Another series of solutions was then prepared by using in each case the same quantity of potassium bromide, as represented in the above formula, but replacing varying quantities of the antimony chloride by equivalent quantities of antimony bromide. The actual weights in grams of salts used in the preparation of these solutions were as follows:

TABLE I.

| | $SbCl_3$. | $SbBr_3$. | KCl. | KBr. |
|---|---|---|---|---|
| B | 40.00 | ... | 30.0624 | 15.156 |
| C | 40.00 | ... | 22.5468 | 27.156 |
| D | 40.00 | ... | 7.5156 | 51.156 |
| E | 40.00 | ... | ... | 63.156 |
| F | 20.00 | 31.80 | ... | 63.156 |
| G | 4.00 | 57.24 | ... | 63.156 |

The weights of the several elements in the above six solutions are as follows:

TABLE II.

| | Sb. | Br. | Cl. | K. | Total. |
|---|---|---|---|---|---|
| B | 21.20 | 10.18 | 33.09 | 20.75 | 85.22 |
| C | 21.20 | 18.23 | 29.53 | 20.75 | 89.71 |
| D | 21.20 | 34.35 | 22.38 | 20.75 | 98.68 |
| E | 21.20 | 42.41 | 18.80 | 20.75 | 103.16 |
| F | 21.20 | 63.61 | 9.40 | 20.75 | 114.96 |
| G | 21.20 | 80.57 | 1.88 | 20.75 | 124.40 |

The solutions were allowed to crystallize slowly by standing in a drying oven. In the oven were placed also shallow vessels containing sulphuric acid. The temperature of the oven was kept constant at 35°. At first crystals of potassium chloride and potassium bromide alone separated from the solutions. Finally crystals were obtained which on being placed in water showed instant decomposition with liberation of white, flocculent antimony oxy-salts. The crystals varied in color from lemon-yellow to colorless, as the proportion of bromine decreased and chlorine increased in the solutions from which they were formed. These solutions showed the same gradation in color. The crystals prepared by using the proportions indicated by Atkinson, $SbCl_3$. $3KBr$, (E), were tetragonal pyramids, and agreed perfectly with the description of Atkinson's compound given by Solly.[1] The

[1] J. Chem. Soc. 1883, 293.

crystals from F were greenish yellow and seeming hexagonal plates superimposed; those from G were bright yellow and showed a well-defined orthorhombic form. On the other hand the crystals from B and C were almost colorless and showed an hexagonal form, while those from D were yellow tetragonal pyramids.

### *Method of Analysis.*

In a weighed portion of the compound, water was determined by loss of weight on standing over phosphorus pentoxide in a desiccator. The dried residue was then dissolved in water acidulated with hydrochloric acid. Into this solution, kept warm, hydrogen sulphide was passed for one hour. During the last fifteen minutes of the passage of the gas the temperature of the solution was raised to gentle boiling. While still hot the solution was tightly corked and allowed to stand one hour. The precipitated antimony sulphide was then filtered on to a Gooch crucible, dried for one hour at a temperature of 110° in a current of dry carbon dioxide, and finally heated for two hours at 210°. This effected the conversion of the antimony sulphide from the red form to the black. In the filtrate, potassium was determined by conversion into the sulphate by means of sulphuric acid, the last traces of which were removed by heating in an atmosphere of ammonia. Another weighed portion of the salt was dissolved in water acidulated with tartaric acid. From this solution bromine and chlorine were precipitated as silver salts, dried, weighed, and finally heated in a current of chlorine gas.

### *Analytical Results.*

I. 0.6230 gram *B* gave 0.2420 gram $Sb_2S_3$ = 0.1727 gram Sb; 0.2963 gram $K_2SO_4$ = 0.1330 gram K.

II. 0.3493 gram *B* gave 0.6417 gram AgBr and AgCl. Transformed into 0.6156 gram AgCl, which gives in original substance 0.0469 gram Br and 0.1314 gram Cl.

III. 0.4986 gram *C* gave 0.1858 gram $Sb_2S_3$ = 0.1326 gram Sb; 0.2253 gram $K_2SO_4$ = 0.1011 gram K.

IV. 0.3891 gram *C* gave 0.6971 gram AgBr and AgCl. Transformed into 0.6528 gram AgCl, which gives in original substance 0.0796 gram Br and 0.1261 gram Cl.

V. 0.3591 gram *D* gave 0.0178 gram $H_2O$, 0.1115 gram $Sb_2S_3$ = 0.0796 gram Sb; 0.1439 gram $K_2SO_4$ = 0.0646 gram K.

VI. 0.3044 gram *D* gave 0.4938 gram AgBr and AgCl. Transformed into 0.4333 gram AgCl, which gives in original substance 0.1087 gram Br and 0.0590 gram Cl.

VII. 0.2181 gram *E* gave 0.0110 gram $H_2O$, 0.0667 gram $Sb_2S_3$ = 0.0476 gram Sb; 0.0809 gram $K_2SO_4$ = 0.0363 gram K.

VIII. 0.9125 gram *E* gave 1.4619 grams AgBr and AgCl. Transformed into 1.2560 grams AgCl, which gives in original substance 0.3700 gram Br and 0.1465 gram Cl.

IX. 0.7966 gram *F* gave 0.2277 gram $Sb_2S_3$ = 0.1625 gram Sb; 0.2818 gram $K_2SO_4$ = 0.1265 gram K.

X. 0.6642 gram *F* gave 1.0704 grams AgBr and AgCl. Transformed into 0.8604 gram AgCl, which gives in original substance 0.3774 gram Br and 0.0454 gram Cl.

XI. 0.5879 gram *G* gave 0.0429 gram $H_2O$, 0.1491 gram $Sb_2S_3$ = 0.1064 gram Sb; 0.1755 gram $K_2SO_4$ = 0.0788 gram K.

XII. 0.4943 gram *G* gave 0.7238 gram AgBr and AgCl. Transformed into 0.5578 gram AgCl, which gives in original substance 0.2983 gram AgBr and 0.0056 gram Cl.

TABLE III.

| | $H_2O$. | Sb. | Br. | Cl. | K. | Total. |
|---|---|---|---|---|---|---|
| B | ... | 27.72 | 13.43 | 37.62 | 21.35 | 100.12 |
| C | ... | 26.59 | 20.46 | 32.41 | 20.28 | 99.74 |
| D | 4.96 | 22.17 | 35.71 | 19.38 | 17.99 | 100.21 |
| E | 5.04 | 21.82 | 40.55 | 16.06 | 16.65 | 100.12 |
| F | ... | 20.40 | 56.82 | 6.84 | 15.88 | 99.94 |
| G | 7.30 | 18.10 | 60.35 | 1.13 | 13.39 | 100.27 |

From the above table it will be seen that the compounds *B*, *C* and *F* which have no water of crystallization are the three which show six-sided, seemingly hexagonal, forms. This lack of water of crystallization in members of a series showing such uniformity in variation in other respects is very peculiar.

Specimens of *B*, *C* and *F* were prepared also by allowing solutions similar to those described in Table I to stand over sulphuric acid in desiccators at the ordinary temperature of the laboratory. The compounds thus formed were tetragonal and showed varying proportions of water of crystallization. The results of analysis of these compounds calculated to a dry basis corresponded closely with those of the anhydrous compounds above. I have not been

able to determine what is the cause of the separation of the anhydrous compound in some cases and the hydrous in others. From the analyses, however, we can conclude that the hexagonal form is characteristic of the anhydrous compound. In order better to compare the analytical results, all have been reduced to a dry basis.

TABLE IV.

| | Sb. | Br. | Cl. | K. | Total. |
|---|---|---|---|---|---|
| B | 27.72 | 13.43 | 37.62 | 21.35 | 100.12 |
| C | 26.59 | 20.46 | 32.41 | 20.28 | 99.74 |
| D | 23.32 | 37.57 | 20.39 | 18.93 | 100.21 |
| E | 22.98 | 42.70 | 16.91 | 17.53 | 100.12 |
| F | 20.40 | 56.82 | 6.84 | 15.88 | 99.94 |
| G | 19.51 | 65.10 | 1.22 | 14.44 | 100.27 |

From the close analogy of these results to those similarly obtained in the mixed halides of lead and potassium, it seemed fair to suppose that these compounds were mixtures of the simple halo-antimonites, and since Poggiale[1] states that the salt $SbCl_3.3KCl$ crystallizes from a solution in water of the two salts in the proportion indicated in the formula, it seemed reasonable to expect that the compounds would be mixtures of the salts $SbCl_3.3KCl$ and $SbBr_3.3KBr$. If, then, we assume *E* to be such a mixture, the amount of antimony required would be 20.20 per cent., but there was found 22.98 per cent.; further 19.78 per cent. of potassium is required, while there was found only 17.53 per cent. Evidently this assumption is wrong.

To gain further knowledge of the nature of these compounds, it was deemed best to prepare the simple double halides at each end of the above series by mixing together the antimony and potassium salts indicated in the formulas $SbCl_3.3KCl$ (Poggiale) and $SbBr_3.3KBr$, dissolving each mixture in hot water and allowing to crystallize by standing in an oven at 35°. From the solution of the chlorides there separated a few columnar, colorless crystals. After removing these, there separated in large quantities six-sided crystals, colorless, and closely resembling the salt $Rb_{12}Sb_{10}Cl_{42}$ described by Saunders.[2] The existence of this rubidium salt has been recently confirmed by Wheeler.[3] The above crystals, labeled *A*, gave on analysis the following results:

[1] Compt. rend. **20**, 1180. [2] This Journal **14**, 161.
[3] Am. J. Sci. [3] **46**, 273.

I. 0.3302 gram *A* gave 0.1398 gram $Sb_2S_3$ = 0.0998 gram Sb; 0.1667 gram $K_2SO_4$ = 0.0748 gram K.

II. 0.3150 gram *A* gave 0.5992 gram AgCl = 0.1482 gram Cl.

| | Found. | Calculated for $K_{22}Sb_{10}Cl_{53}$. | Calculated for $K_3SbCl_6$ (Poggiale). |
|---|---|---|---|
| Sb | 30.22 | 30.14 | 26.64 |
| Cl | 47.05 | 47.24 | 47.28 |
| K | 22.66 | 22.62 | 26.08 |
| | 99.93 | 100.00 | 100.00 |

The atomic ratio of antimony to potassium is found from the above results of analysis to be

Sb : K as 1 : 2.297,

giving thus the formula $10SbCl_3.23KCl$, and not $SbCl_3.3KCl$ as stated by Poggiale. From the solution of the bromides there separated at first a few small crystals of potassium bromide; after removing these from the solution, beautiful transparent yellow crystals, possessing a well-defined orthorhombic form, were deposited. These crystals were much larger than those formed from the solution of the chlorides. They were labeled *H*. On analysis the following results were obtained:

I. 0.4830 gram *H* gave 0.0351 gram $H_2O$; 0.1207 gram $Sb_2S_3$ = 0.0861 gram Sb; 0.1443 gram $K_2SO_4$ = 0.0648 gram K.

II. 0.5433 gram *H* gave 0.7858 gram AgBr = 0.3344 gram Br.

| | Found. | Calculated for $K_{22}Sb_{10}Br_{53}.27H_2O$. | Found. Calculated to dry basis. | Calculated for $K_{22}Sb_{10}Br_{53}$. |
|---|---|---|---|---|
| $H_2O$ | 7.27 | 7.12 | ... | ... |
| Sb | 17.83 | 17.57 | 19.22 | 18.92 |
| Br | 61.55 | 62.12 | 66.38 | 66.88 |
| K | 13.42 | 13.19 | 14.47 | 14.20 |
| | 100.07 | 100.00 | 100.07 | 100.00 |

The atomic ratio of antimony to potassium in the dried salt is,

Sb : K as 1 : 2.31,

giving thus the formula $10SbBr_3.23KBr$.

Knowing now the character of the simple salts formed at each end of the series, and assuming the intermediate compounds to be mixtures of these two, we should find:

TABLE V.

| | Antimony. | | Potassium. | |
|---|---|---|---|---|
| | Found. | Required. | Found. | Required. |
| B | 27.72 | 27.80 | 21.35 | 20.86 |
| C | 26.59 | 26.47 | 20.28 | 19.86 |
| D | 23.32 | 23.64 | 18.93 | 17.74 |
| E | 22.98 | 22.87 | 17.53 | 17.17 |
| F | 20.40 | 20.43 | 15.88 | 15.34 |
| G | 19.51 | 19.20 | 14.44 | 14.40 |

Atkinson deduced his formulas for these compounds from determinations of bromine and chlorine alone. That these data are not sufficient for calculating formulas for these compounds will readily be seen from the following:

Chlorine per cent. calculated for:

$K_3SbCl_6 = 47.28$
$K_{22}Sb_{10}Cl_{52} = 47.24$
$KCl = 47.54$
$SbCl_5 = 47.01.$

Bromine per cent. calculated for:

$K_3SbBr_6 = 66.91$
$K_{22}Sb_{10}Br_{82} = 66.88$
$KBr = 67.14$
$SbBr_3 = 66.67.$

That the compounds are mixtures and not true salts is rendered still more probable by a comparison of the composition of the compounds and the solutions from which they were formed. The composition of the solutions, reduced to a basis of parts in one hundred for the sake of comparison with the percentage composition of the compounds, is as follows:

TABLE VI.

| | Sb. | Br. | Cl. | K. |
|---|---|---|---|---|
| B | 24.87 | 11.95 | 38.83 | 24.35 |
| C | 23.63 | 20.32 | 32.92 | 23.13 |
| D | 21.48 | 34.81 | 22.68 | 21.03 |
| E | 20.55 | 41.11 | 18.23 | 20.11 |
| F | 18.44 | 55.33 | 8.18 | 18.05 |
| G | 17.04 | 64.77 | 1.51 | 16.68 |

That the compounds should show a slightly larger percentage foantimony and smaller percentage of potassium than the solu-

tions from which they were formed is to be expected in the light of the fact already mentioned, that, when the solutions were allowed to stand, potassium bromide and chloride first separated in small quantities, then came the mixed double halides. Again, if we tabulate the variations of the percentages of bromine and chlorine in the series of salts on the one hand, and in the series of solutions on the other, we find:

TABLE VII.

| | Bromine. | | Chlorine. | |
|---|---|---|---|---|
| | Solution. | Salt. | Solution. | Salt. |
| B–C | 8.37 | 7.03 | 5.91 | 5.21 |
| C–D | 14.49 | 17.11 | 10.24 | 12.02 |
| D–E | 6.30 | 5.13 | 4.45 | 3.48 |
| E–F | 14.22 | 14.12 | 10.05 | 10.07 |
| F–G | 9.44 | 8.28 | 6.67 | 5.62 |

*Effect of Heat upon the Mixtures.*

Atkinson states that if the compound $SbCl_3.3KBr.1\frac{1}{2}H_2O$ be heated to 300°, all antimony is volatilized as halogen salts, while chlorine and bromine remain in the residue combined with potassium in equal atomic proportions. No analytical results are given. Hoping to obtain a simple method for the determination of potassium in the compounds, and also to gain further evidence as to the character of the compounds experiments were made with B and F. Specimens of these were slowly heated to 300° and kept at this temperature two hours. On reheating for one hour at 300° no further loss of weight occurred. The residues were then dissolved in water, and the halogens determined by precipitation with silver nitrate. In this way results were obtained which showed rough agreement with those required by calculation, if it be assumed that the compounds are mixtures. But on removing the excess of silver from the filtrates, and passing hydrogen sulphide through, a decided precipitate of antimony sulphide was observed, showing that though a constant weight had been obtained, there still remained portions of antimony salts in the residue. For this reason the bromine and chlorine results in the residues cannot be used as satisfactory evidence as to the nature of the compounds. In a general way, however, they tend to confirm the view that the compounds are mixtures of the halo-antimonites containing only one halogen.

The evidence obtained in this investigation, taken in connection with that obtained in the case of the mixed double halides of lead and potassium, seems to show that these compounds of Atkinson are not true salts, but isomorphous mixtures of the simple halo-antimonites.

Mr. H. Hillyer is now at work, in this laboratory, upon Pitkin's[1] so-called salt, $PtCl_4.2KBr$. I expect to begin work at once upon mixed double halides in which potassium is replaced by such a base, for example, as aniline.

In a recent article[2] I described certain green tabular crystals formed by dissolving lead iodide in dilute solutions of potassium bromide and allowing the solutions to crystallize. At the time of the publication of that article, only one type of potassium halo-plumbite was known, namely, $KPbX_3$. Analyses of these green crystals led me to the conclusion that they were mixtures of $KPbI_3$, $KPbBr_3$ and $PbBr_2$. Since that time Wells[3] has prepared a salt to which he ascribes the formula $KPb_2Br_5$. In a later article[4] he puts forward the view that the green tabular crystals which I had prepared were mixtures of $KPb_2Br_5$ and $KPb_2I_5$, and not of $KPbI_3$, $KPbBr_3$ and $PbBr_2$. I must confess that I consider his view much more plausible than mine. So far as agreement between theoretical and analytical results is concerned, one view is practically as good as the other. Other reasons, however, tend to show the correctness of his interpretation of the analytical results. In the first place, there is great crystallographic similarity between the salt $KPb_2Br_5$ and the green tabular crystals. In the second place, the conception of "free lead bromide" in the crystals necessitates, as Wells observes, the assumption of the isomorphism of lead bromide with $KPbI_3$ and $KPbBr_3$. While this is not impossible, yet it is much more improbable than the assumption of the isomorphism of $KPb_2Br_5$ and $KPb_2I_5$. Of greater importance still is the fact that though repeated efforts were made to obtain crystals containing very small or very large proportions of "free lead bromide," in no case did the proportion fall below 30 per cent. of the weight of the crystal, or exceed 36 per cent. This constancy is hardly to be expected if "free lead bromide" is present in the crystals.

UNIVERSITY OF GEORGIA, *July* 13, 1894.

[1] J. Am. Chem. Soc. **1**, 472.
[2] This Journal **15**, 97.
[3] Am. J. Sci. 1893, **45**, 134.
[4] *Ibid.* 1893, **46**, 38.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

# XI.—CAMPHORIC ACID.[1]

## SECOND PAPER.

BY W. A. NOYES.

In the first paper[2] a $\beta$-camphoraminic acid, obtained by the action of caustic soda on camphoric imide, was described. I have since learned that this compound had been previously described by Hoogewerf and Van Dorp in the Proceedings of the Dutch Academy of Science for January 27th, 1894. These authors do not give the melting-points of the two camphoraminic acids, but establish the isomerism of the bodies on the rotatory power and on the conversion into two cyan-lauronic acids, $C_8H_{14}\begin{cases}CN\\CO_2H.\end{cases}$ This last name is based on the relation between the formula of these acids and that of the lauronolic acid of Fittig and Woringer.[3] At that time these acids might with equal propriety be referred either to lauronolic acid or to the isomeric campholytic acid of Walker.[4] Since, however, as will be shown in this paper, one of these acids is closely related to campholytic acid while the other is probably closely related to lauronolic acid, it seems desirable to express these facts in the names of the bodies. I would therefore suggest that the following nomenclature be followed for the present. The two carboxyl groups of camphoric acid and the corresponding positions of other groups are distinguished as $\alpha$ and $\beta$.

$\alpha$-Camphoraminic acid, $C_8H_{14}\begin{cases}CONH_2\ \alpha\\CO_2H\ \beta\end{cases}$,

$\beta$-Camphoraminic acid, $C_8H_{14}\begin{cases}CO_2H\ \alpha\\CONH_2\ \beta\end{cases}$,

Cyan-lauronic acid,[5] $C_8H_{14}\begin{cases}CN\ \alpha\\CO_2H\ \beta\end{cases}$,

Dihydro-cyan-campholytic acid,[5] $C_8H_{14}\begin{cases}CO_2H\ \alpha\\CN\ \beta\end{cases}$,

[1] Communicated to the American Association for the Advancement of Science at the Brooklyn meeting.

[2] This Journal **16**, 307.

[3] Ann. Chem. (Liebig) **227**, 6.

[4] J. Chem. Soc. **63**, 498.

[5] Hoogewerf and Van Dorp: *Loc. cit.*

Amino-lauronic acid,[1] $C_8H_{14}<^{NH_2\ \alpha}_{CO_2H\ \beta}$,

Dihydro-amino-campholytic acid,[2] $C_8H_{14}<^{CO_2H\ \alpha}_{NH_2\ \beta}$,

Campholytic acid, $C_8H_{13}CO_2H\ \alpha$

Lauronolic acid, $C_8H_{13}CO_2H\ \beta$.

Since, as will be shown below, the camphoraminic acid of Claissen and Manasse[3] is the $\alpha$-acid, we have for camphor the relation $C_8H_{14}<^{CH_2\ \alpha}_{CO\ \beta}$, and, since Walker obtained his campholytic acid from the ortho-ethyl ester of camphoric acid, this ester must have the relation $C_8H_{14}<^{CO_2C_2H_5\ \alpha}_{CO_2H\ \beta}$.

### *Preparation of Camphoric Acid.*

Considerable experience has been gained in the preparation of camphoric acid, and some of its more common derivatives, and some of the methods used may be of interest to other workers in this field. For the preparation of camphoric acid 150 grams of camphor with 1200 cc. of nitric acid (1.42) and 800 cc. of water were placed in a three-liter flask having a wide test-tube filled with water fitting closely in its neck. The flask was then heated continuously on a steam-bath for 60 to 65 hours, or until a small portion of the liquid, after cooling and saturating with ammonia, left but a small amount of camphor undissolved. Instead of evaporating the nitric acid as directed in Beilstein's Handbook, it is found better to cool the acid thoroughly and filter off the camphoric acid which separates. The latter is washed with water, the washings being kept separate from the nitric-acid mother-liquors. The camphoric acid weighed 93.2 grams. The nitric-acid mother-liquors measured 1800 cc. and had a specific gravity of about 1.26. To these were added 250 cc. of strong nitric acid (1.42) and 150 grams of camphor, and the oxidation and separation of camphoric acid effected as before. This time 116.7 grams of the acid were obtained. To the nitric-acid mother-liquors, measuring 1900 cc., 400 cc. of strong acid were added, bringing the sp. gr. up to 1.28 to 1.29. With this solution 171 grams of camphor were oxidized, giving 121.3 grams of camphoric acid. In all 331 grams of camphoric acid were obtained from 471 grams of camphor, or 70 per cent. of the weight of camphor used.

[1] This paper. [2] This Journal **16**, 310. [3] Ann. Chem. (Liebig) **274**, 71.

*Camphoric Anhydride.* — The camphoric acid obtained as described contains a small amount of camphor and possibly some other impurities, but is sufficiently pure for the preparation of the anhydride. For this purpose 100 grams of the anhydride are mixed with 75 cc. of acetic anhydride, or perhaps better with 65 cc. of the anhydride and 10 cc. of acetyl chloride, and boiled with an inverted condenser for half an hour. After cooling, the anhydride was washed with water and recrystallized from hot alcohol, using the mother-liquors over repeatedly. From 80 to 85 grams of the pure crystallized anhydride were obtained.

*Camphoric Imide.*—50 grams of finely crystalline camphoric anhydride and 125 cc. of alcohol are placed in a 500-cc. distilling bulb, and the ammonia obtained by heating 75 cc. of strong ammonia (0.90) with a reversed condenser is passed into the mixture until all of the anhydride passes into solution and a considerable amount of the ammonia passes through unabsorbed. The bulb is then connected with a condenser and its contents distilled rapidly over the free flame till the boiling-point of the imide is reached. Just at the close of the distillation a considerable amount of the imide condenses in the tube of the distilling-bulb, and it is best to loosen the cork for fear of explosion. The contents of the bulb is poured immediately into a mortar, and when cold, the solid mass is broken up and dissolved in a cold ten-per cent. solution of caustic soda. After filtering, the imide is precipitated as quickly as possible by a rapid current of carbon dioxide. After filtering off and washing there were obtained 30 grams of the pure imide, or about 60 per cent. of the weight of the anhydride taken. From the alkaline filtrate from the imide, hydrochloric acid precipitates a mixture of camphoric acid and camphoraminic acids. This mixture may be treated with acetic anhydride, and from the resulting product a new portion of imide can be obtained, raising the total yield to perhaps 70 or 75 per cent. of the theoretical.

*α-Camphoraminic Acid.*—25 grams of camphoric anhydride are placed in a flask with 50 cc. of alcohol, and ammonia is passed in exactly as in the preparation of the imide. The solution is then poured out into a beaker and allowed to stand until the ammonium salt of the camphoraminic acid has separated as far as possible. The mother-liquors are then removed as far as possible by means of the pump and the salt dried on a porous plate. The salt is then dissolved in a small amount of water, and the cam-

phoraminic acid precipitated by a little more than the theoretical amount of hydrochloric acid. The acid should be added slowly, and care should be taken to secure the separation of the camphoraminic acid in the crystalline form by adding a small amount of the crystalline acid. 100 grams of the anhydride gave 51 grams of the acid melting at 167°–170°. This is sufficiently pure for the preparation of amino-lauronic acid, as the purification of the latter is more easily effected than that of the camphoraminic acid. The alcoholic mother-liquors may be used to prepare the imide as directed above.

*β-Camphoraminic Acid.*—25 grams of the imide are dissolved in 80 cc. of 15 per cent. caustic soda, and the solution heated on the water-bath for an hour and a half. On cooling, and especially on the addition of a fragment of the β-acid, the sodium salt, which is rather difficultly soluble in caustic soda, separates and is filtered off and sucked as dry as possible with the pump. The salt is then dissolved in a small amount of water and the acid precipitated with hydrochloric acid, using the same precautions as with the α-acid. The yield is about 15 grams of an acid melting at 179°–181° and sufficiently pure for conversion into the dihydro-amino-campholytic acid. The alkaline mother-liquors contain some of the α-acid.

### *Dihydro-amino-campholytic Acid.*

The preparation of this acid from camphoric imide was described in the first paper.[1] The method there described gives a pure acid. The mother-liquors, however, contain a small amount of the amino-lauronic acid, which can be separated and identified in the form of its chloride, which melts at 303°–305° and crystallizes in a quite different manner from the chloride of the dihydro-amino-campholytic acid. For the preparation of the latter it is better, therefore, to use the comparatively pure β-camphoraminic acid prepared as described above.

19.9 grams (1 molecule) of the β-camphoraminic acid are dissolved in 100 cc. of 10-per cent. caustic soda. 5.1 cc. or 16 grams of bromine (1 molecule) are dissolved by shaking quickly with 140 cc. of 10-per cent. caustic soda, and the solution added to that first mentioned. Considerable heat is evolved by the reaction and the temperature rises spontaneously about 32°. The solution

[1] This Journal **16**, 310.

is then heated on the water-bath to about 75° for 15 to 20 minutes. After cooling, a little sodium sulphite is added, and the solution is neutralized with hydrochloric acid till a few drops develop no color on boiling in a test-tube with phenol-phthalein. The solution is then evaporated and the amino acid separated by crystallization, and purified by recrystallization from water.

The *chloride* of dihydro-amino-campholytic acid crystallizes from concentrated solutions, on cooling, in long, thick needles which melt with decomposition at 261°–262°. The crystals show no tendency to a concentric grouping, and in this respect differ very markedly from those of the chloride of the isomeric amino-lauronic acid.

0.1909 gram of the salt gave 0.1322 gram AgCl, corresponding to 17.13 per cent. of chlorine. Theory requires 17.11 per cent.

The *nitrate* crystallizes in long needles which melt with decomposition at 212°–213°.

The *chloroplatinate* is very easily soluble in water, and separates, on slow evaporation of its solution, in dark orange-yellow plates, sometimes of considerable size.

0.2239 gram of the salt gave 0.0581 gram Pt, or 25.95 per cent. Theory requires 25.93 per cent.

*Anhydride of Dihydro-amino-campholytic Acid.*

An attempt was made to obtain an amine by distilling dihydro-amino-campholytic acid with quicklime. The lime acts, instead, as a dehydrating agent, and an inner anhydride of the acid is formed. If a little care is taken to avoid too high a temperature the reaction is almost quantitative, and the nearly pure anhydride condenses in the front part of the tube as a white, waxlike solid. The substance is best purified by crystallization from a very small amount of warm ligroin. The crystals which separated from the concentrated solution on cooling were separated from the mother-liquors by spreading them on a porous plate. The crystallized substance retains it waxlike character, but melts sharply at 188°–189°. It boils without decomposition at 285°–287°. The substance is indifferent and is very easily soluble in water, alcohol, benzene, chloroform, ether and carbon bisulphide.

0.1596 gram of the substance gave 0.1426 gram $H_2O$ and 0.4120 gram $CO_2$.

0.1153 gram gave 0.01065 gram N.

| | Calculated for $C_8H_{14}<^{CO}_{NH}>$. | Found. I. | II. |
|---|---|---|---|
| C | 70.59 | 70.40 | ... |
| H | 9.80 | 9.92 | ... |
| N | 9.15 | ... | 9.24 |

Attempts to obtain an amine by the distillation of dihydro-amino-campholytic acid with barium hydroxide, with soda-lime, and with sodium methylate, were unsuccessful. In some cases very considerable amounts of permanent gases were formed, and it was evident that the reaction consisted chiefly in a decomposition of the substance in a manner which would not yield any simple derivatives of the acid.

### *Campholytic Acid.*[1]

When dihydro-amino-campholytic acid is dissolved in the calculated amount of sulphuric acid, and sodium nitrite is added to the solution, decomposition begins at once, accompanied by a rise of temperature. The acid is best separated from the solution by distillation with a current of steam. It partly separates from the distillate in oily drops which are very slightly heavier than water. The acid may be separated from the distillate by extraction with ether, or it may be converted into the sodium salt by means of sodium carbonate and the solution evaporated, apparently without any decomposition. The free acid boils at 240°–243°. When treated with bromine in carbon-disulphide solution the acid yields a dibromide which melts, when heated quickly, at 113°–114°. Walker[2] gives the melting-point of the dibromide of campholytic acid as 110°, but states that it depends somewhat on the manner of heating, and in a private communication states that in one case a melting-point of 115° was observed. My dibromide shows the same tendency to blacken when exposed to the light which was observed by Walker. It also decomposes with ammonia or sodium carbonate, forming an oil which is insoluble both in acids and bases. The barium salt remains on evaporation as a sticky mass. The only respect in which my acid appears to differ essentially from that of Walker seems to be in that mine gives precipitates when zinc chloride or silver nitrate is added to a solution of its sodium salt, while Walker states that the ammonium salt of his

[1] Dr. Walker writes me that he is at present interested n other matters and has very kindly left the further study of this substance to me.

[2] J. Chem. Soc. **63**, 499 (1893).

acid gives no precipitate with salts of the heavy metals. The difference is probably due to his use of the ammonium salt instead of the sodium.

*Zinc Campholytate.*—This salt was prepared by adding a solution of zinc chloride to a solution of the sodium salt of campholytic acid. It separates in a semi-crystalline form, and is very difficultly soluble in water. It is easily soluble in ether.

0.2015 gram of the salt gave 0.0445 gram of zinc oxide.

| | Calculated for $(C_9H_{13}CO_2)_2Zn$. | Found. |
|---|---|---|
| Zn | 17.52 | 17.72 |

An attempt to remove four hydrogen atoms from campholytic acid by oxidation with potassium ferricyanide, a method which has been successful with dihydro- and tetrahydro-terephthalic acids,[1] gave a negative result. The acid appears to remain unchanged.

The study of the acid in other directions will be continued.

## *Amino-lauronic Acid.*[2]

When $\alpha$-camphoraminic acid is treated with sodium hypobromite, it is converted into amino-lauronic acid in the same manner in which the $\beta$-acid is converted into dihydro-amino-campholytic acid. Instead of exactly neutralizing the solution and attempting to separate the free acid, it is better, however, to render the solution strongly acid with hydrochloric acid and evaporate till the chloride of the acid begins to separate. On cooling most of the chloride will separate from the solution together with some sodium chloride. It may be purified by recrystallization from water.

It is very noticeable that in the treatment of $\alpha$-camphoraminic acid with sodium hypobromite the rise in temperature is very

[1] Ann. Chem. (Liebig) **358**, 2 and 49.

[2] In a private communication from Professor W. A. Van Dorp he tells me that he and Professor Hoogewerf have prepared amino-lauronic acid, the work having been done before my first paper appeared. As they have not yet published anything on the subject, they have very kindly left the further study of the acid and its decomposition-products to me. On account of their work, the study of the amino-lauronic acid itself has been carried no further than was necessary in connection with the other work described in this paper. Professor Van Dorp gives the melting-point of the free amino-lauronic acid as 260°, and that of its anhydride as 204°–206°, a little higher than found by myself. They have also prepared the following compounds:

$(C_9H_{17}NO_3)_2H_2PtCl_6$,
$(C_9H_{17}NO_3)HCl.AuCl_3$,
$C_9H_{16}AgNO_3$,
$C_9H_{17}NO_3.C_6H_3(NO_2)_3OH$,
$C_9H_{16}NO_3.C_6H_5CO$—melts at 206°.

much less than when β-camphoraminic acid is treated in the same manner. In the case of the β-acid the rise in temperature is about 32°, while with the α-acid it is only about 15°. Dr. Claissen very kindly sent me a specimen of the camphoraminic acid obtained by the action of hydrochloric acid on iso-nitroso camphor.[1] When one gram of this acid was treated with caustic soda and sodium hypobromite in the proportions given, the rise in temperature was 13°. From the solution, the chloride of amino-lauronic acid, crystallizing in its characteristic forms and melting at 303°–305°, was readily obtained. Since in Claissen's acid, unless we suppose the reactions to be accompanied by a deep-seated rearrangement of the molecule, which seems highly improbable, the amido group must be combined with the same carbon atom which is in the methylene group of camphor, these facts establish the correspondence of that methylene group with the amidic group of α-camphoraminic acid, and the correspondence of the carbonyl of camphor with the amidic group of the β-acid.

The *chloride* of amino-lauronic acid crystallizes in needles which have a strong tendency to a concentric grouping. It appears to be less easily soluble than the isomeric chloride of dihydro-amino-campholytic acid. It melts at 303°–305°.

The *chloroplatinate* crystallizes in light orange-yellow granular crystals which under a glass are seen to consist of small plates, some of them in well-shaped six-sided forms. The salt is very much less easily soluble in water than that of the isomer.

0.1416 gram of the salt gave 0.0368 gram Pt.

| | Calculated for $(C_8H_{14}{<}^{CO_2H}_{NH_2})_2H_2PtCl_6$. | Found. |
|---|---|---|
| Pt | 25.93 | 25.99 |

*Anhydride of Amino-lauronic Acid.*

This was obtained by mixing the chloride of amino-lauronic acid with an excess of quicklime and distilling. The substance was purified by crystallization from ligroin. It resembles the isomer in almost every particular except the melting-point. It melts at 203°.

0.1291 gram gave 0.01188 gram N.

| | Calculated for $C_8H_{14}{<}^{CO}_{NH}{>}$. | Found. |
|---|---|---|
| N | 9.15 | 9.20 |

[1] Ann. Chem. (Liebig) **274**, 79.

The study of the products of the decomposition of amino-lauronic acid when its chloride is heated with a solution of sodium nitrite is not yet satisfactorily completed, but, as the further study of the subject is likely to take a considerable amount of time, it seems desirable to give here a brief statement of the results already obtained. The products of the decomposition appear to be much more complex than in the case of dihydro-amino-campholytic acid. An unsaturated acid is formed which resembles very closely the lauronolic acid of Fittig and Woringer.[1] The acid gives with fuming hydrobromic acid a crystalline but extremely unstable hydrobromide. The calcium salt of the acid separates on the surface of its solution during evaporation in dendritic forms, as observed by Woringer. It contains, however, two, instead of three, molecules of water. On account of this difference the two acids cannot be said to be identical, but, until a further comparison has been made, it does not seem best to give the acid a new name. Attempts to obtain a salt with a different amount of water, by evaporating the solution at a low temperature, were not successful.

0.0638 gram of salt lost 0.0058 gram $H_2O$ at 135° and gave 0.0226 gram $CaSO_4$.

0.1270 gram of the salt lost 0.0113 gram $H_2O$ at 135°.

0.1074 gram of the salt lost 0.0102 gram $H_2O$ at 135° and gave 0.0381 gram $CaSO_4$.

| | Calculated for $(C_8H_{13}CO_2)_2Ca + 2H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| $2H_2O$ | 9.42 | 9.09 | 8.90 | 9.50 |
| Ba | 10.47 | 10.42 | ... | 10.43 |

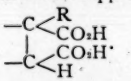
Solutions of the sodium salt of the acid give precipitates with zinc chloride and with silver nitrate. The zinc salt is easily soluble in ether.

Besides the unsaturated acid there is, in the decomposition of the amino-lauronic acid, an evolution of carbon dioxide and the formation of a hydrocarbon which boils at about 120°, but which has not yet been obtained in sufficient amount for identification. It is probably tetra-hydroxylene. There is also formed a small amount of a body which conducts itself like a lactone and which is probably the campholactone of Woringer. It is insoluble in a solution of sodium carbonate, but dissolves in a solution of barium hydroxide, and is regenerated by acidifying the solution with

[1] Ann. Chem. (Liebig) **227**, 7.

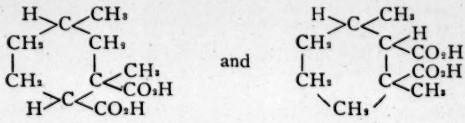
hydrochloric acid and distilling. It solidifies at a low temperature, but it has not been obtained in sufficient amount to purify the body and obtain a satisfactory melting-point.

The experiments described in this paper cannot be said to lead to any positive conclusion with regard to the structure of camphoric acid. They do furnish, however, an interesting confirmation of the conclusions arrived at by Walker.[1] All of the observations made by myself, as well as those made by Walker, agree best with the supposition that camphoric acid contains the complex



According to this formula the carboxyl group written below is retained in campholytic acid, while that written above is retained in the other unsaturated acid. In campholytic acid the double union would be between the two carbon atoms with which the two carboxyl groups of the camphoric acid are connected, while in the isomeric acid the double union cannot occupy that position, but must be between the two carbon atoms which occupy the $\beta$ and $\gamma$ positions with regard to the carboxyl of that acid. Such a position for the double unions in the two cases readily explains the formation of a lactone and a hydrocarbon in the case of the isomeric (lauronolic?) acid. In the case of campholytic acid the formation of such bodies is very trifling, if it occurs at all. The ease with which each amino acid forms an anhydride, and the fact that only one readily forms a lactone, is a further indication that the hydroxyl of the acid corresponding to the lactone does not occupy the same position as the amine group of the amino acid.

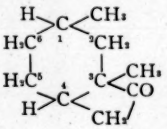
If we accept the formation of hexahydro-metaxylene from camphoric acid[2] as proof that the skeleton of metaxylene already exists in the acid, there are left, apart from stereometric isomerism, but two possibilities for the formula of the acid which satisfy the conclusions reached above. These are:



[1] J. Chem. Soc. **63**, 506 (1893).

[2] Wreden: Ber. d. chem. Ges. **6**, 1379; Wallach: *Ibid.* **25**, 923.

The latter of these formulæ was proposed by Collie,[1] and has been referred to as satisfactorily explaining the results of his work, by Walker.[2] So far as his results and my own are concerned, the two formulæ are equally satisfactory. In relation to camphor, however, the first formula seems to be more satisfactory. It is closely related to a formula for camphor proposed by Armstrong,[3] and more recently referred to by Wallach,[4] who favors this formula for camphoric acid:



Everything points to such a close relationship as this formula supposes to exist between camphor and camphoric acid. Especially the conversion of camphor into iso-nitroso camphor and *a*-camphoraminic acid,[5] and the formation of camphor chinon and camphoric acid from camphor-carboxylic acid,[6] are scarcely consistent with any considerable rearrangement of the molecule in the conversion of camphor into camphoric acid. Aschan[7] favors this conclusion.

This formula also gives a more satisfactory explanation of the formation of cymene from camphor than most of the formulæ which have been proposed. If we suppose the ring to separate between the carbon atoms numbered 1 and 2, it might easily be reformed between the carbonyl of the camphor and the carbon atom numbered 1. Such a formation of rings under the influence of a carbonyl or aldehyde group has been frequently observed of late. If at the same time there occurs a separation between the carbon of the carbonyl group and the carbon atom numbered 3, there would be formed the skeleton of cymene.

Aschan[8] has objected to Bredt's formula for camphoric acid that the bromine of brom-camphoric anhydride cannot be removed, except by reagents which cause the opening of the anhydride ring, while in many other cyclic compounds bromine is easily

[1] Ber. d. chem. Ges. **25**, 1116.
[2] Ber. d. chem. Ges. **16**, 2260.
[3] Claissen and Manasse: Ann. Chem. **274**, 71.
[4] *Loc. cit.*
[5] J. Chem. Soc. **63**, 510 (1893).
[6] *Ibid.* **25**, 921.
[7] Aschan: Ber. d. chem. Ges. **27**, 1448.
[8] Ber. d. chem. Ges. **27**, 1441.

removed along with the hydrogen combined with an adjacent carbon atom. The same objection, if valid, would apply to the formula here proposed. It seems possible, however, that the presence of the anhydride ring gives such a configuration to the molecule that the removal of bromine and hydrogen with the establishment of a double union is impossible. So far as I am aware, no observations with compounds of known structure which would have a bearing on this question are known.

It is hoped that a further study of some of the compounds described in this paper may lead to more positive evidence of the truth or falsity of these formulæ.

In conclusion it may be worth while to remark that the relative positions of the carbonyl and methylene groups in Armstrong's formula for camphor are in accordance with conclusions reached in the first part of this paper.

A small portion of the experimental work described in this paper was done by Dr. H. H. Ballard and Mr. Elmer Brown, to whom I wish to express my sincere thanks.

TERRE HAUTE, *June* 29, 1894.

## THE ELECTROLYTIC REDUCTION OF PARANITROBENZOIC ACID IN SULPHURIC-ACID SOLUTION.

BY A. A. NOYES AND A. A. CLEMENT.

In an article published some time ago[1] we showed that, when nitrobenzene in sulphuric-acid solution is submitted to the action of electrolytic hydrogen, the resulting product is not aniline, but the sulphonic acid of paramidophenol. That this reaction is characteristic of nitro compounds in general has since been proved by Gattermann,[2] who investigated a great variety of them —nitro-hydrocarbons, nitro-anilines, and nitro-acids—and found them all to undergo change in a similar way, the reduction of the nitro group being accompanied by a migration of one of its oxygen atoms to the para position. Only those compounds in which the para position is already occupied by another element

[1] Ber. d. chem. Ges. **26**, 990. [2] *Ibid.* **26**, 1844.

or group than hydrogen form exceptions to this rule. Of such compounds only two were investigated—paranitroorthotoluidine and paranitrotoluene. The reduction-product of the former consisted of diamido-cresol [$CH_3(1)NH_2(2)NH_2(4)OH(5)$], a migration of an oxygen atom to the *ortho* position having taken place. In the second case there was obtained a complex body which was shown[1] to result from the condensation of the primary reduction-product, amidobenzyl alcohol, with a second molecule of nitrotoluene; thus, in this case, substitution of hydroxyl in the (methyl) group occupying the para position occurs. What reaction takes place seems therefore to depend on the nature of the para group, and the investigation of other para compounds in this direction is of considerable interest. We wish to describe here the reduction-product of one of these, *i. e.*, of paranitrobenzoic acid. We expected to obtain from it amidooxybenzoic acid, or possibly amidobenzoic acid itself; but, remarkably enough, neither of these substances is formed.

The paranitrobenzoic acid used was prepared[2] by boiling for one hour with return-cooler portions of 20 grams of paranitrotoluene with 60 grams of potassium permanganate dissolved in two liters of water, filtering out the precipitate, concentrating the filtrate, and acidifying it. In this way 18 grams, 73 per cent. of the theoretical yield, were obtained.

The apparatus used for the electrolysis consisted of a small beaker, to the sides of which a large platinum electrode was closely fitted, and in which was placed a porous cup containing sulphuric acid and a small platinum electrode to serve as the positive pole. The solution, made by dissolving 12 grams of the nitrobenzoic acid in 100 grams of warm concentrated sulphuric acid, was poured into the beaker, which was surrounded with asbestos to prevent loss of heat, and a current of one ampere passed through for twenty-four hours.

To isolate the product, the solution was diluted with water, cooled, and filtered. The precipitate was found to be very little soluble even in boiling water, showing the absence of sulphates of bases. It was treated with sodium-carbonate solution, the residue consisting of sulphur was filtered out, and the filtrate was acidified. A voluminous precipitate separated; it was collected on a filter, and washed, first with water, then with alcohol and ether, to

[1] Ber. d. chem. Ges. **26**, 2810. [2] *Ibid.* **10**, 580.

remove any unchanged nitrobenzoic acid. Four grams of product were thus obtained. Its properties and analysis showed it to be paramidophenolsulphonic acid. It was only very slightly soluble in boiling water and is insoluble in alcohol and ether. It reduced silver nitrate solution in the cold, with production of a purple color. The solution of its salts turned brown rapidly in the air. It gave the following results on analysis:

| | Found.[1] | Calculated for $C_6H_3.NH_2.OH.SO_3H$. |
|---|---|---|
| C | 37.70 | 38.09 |
| H | 3.75 | 3.70 |
| $SO_3$ | 42.40 | 42.33 |

To give further proof of the identity of the acid, some of it was heated to 175° in a closed tube with concentrated hydrochloric acid. At this temperature the sulphonic group was split off, as is the case with the paramidophenolsulphonic acid.[2] The hydrochlorate, which crystallized out on cooling, was filtered off, dried, and boiled with a large excess of acetic anhydride. The resulting product after crystallization from water showed a melting-point of 152°, identical with that of diacetylparamidophenol.

The electrolytic reduction-product of paranitrobenzoic acid is therefore paramidophenolsulphonic acid, the tendency of the oxygen atom to assume the para position being great enough to expel the carboxyl group originally occupying it.

Massachusetts Institute of Technology, Boston, *June*, 1894.

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## INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS.

### III.—PHTHALEÏNS OF ORTHO-SULPHO-PARA-TOLUIC ACID.[3]

By James A. Lyman.

Ortho-sulpho-para-toluic acid was made according to the method described by Randall,[4] from methyl-saccharin that had

[1] 0.3964 gram substance gave 0.5479 gram $CO_2$ and 0.1336 gram $H_2O$; 0.4356 gram substance gave 0.5380 gram $BaSO_4$.

[2] Ber. d. chem. Ges. **26**, 992.

[3] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1892.

[4] This Journal **13**, 256.

been placed at the disposal of Prof. Remsen by the "Badische Anilin- und Soda-fabrik." The methyl-saccharin in portions of 25 grams was boiled in a flask fitted with a reflux condenser with a mixture of 100 cc. of concentrated hydrochloric acid and 500 cc. of water. After boiling for two hours, all the sulphinide had been transformed, and the solution was then decolorized and evaporated to crystallization.

The acid ammonium salt may be converted by treatment with phosphorus pentachloride directly into the chloride of the acid; but as some of the chlor-phosphuret of nitrogen, $P_3N_3Cl_6$, is always formed,[1] it was found best first to make the neutral potassium salt and to make the chloride from this. By boiling the chloride with water, ortho-sulpho-para-toluic acid is formed.

In the preparation of the phthaleïns care must be taken that the ortho-sulpho-para-toluic acid used is anhydrous, as the presence of water seems to promote the formation of tar-like substances. The acid is best dehydrated by long heating below 135°; it should not be allowed to melt.

The best method of analysis of the products was found to be the burning in a platinum boat in a stream of oxygen, the front half of the tube being filled with chromate mixture.

### *Action of Phenol.*

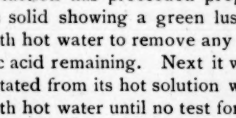
*Phenol-para-methyl-sulphon-phthaleïn.*—Carefully dehydrated ortho-sulpho-para-toluic acid and dry, crystallized phenol in the proper molecular proportion (1 to 2) are heated together in a glass tube closed at one end. The glass tubing is used in preference to a test-tube on account of its greater strength. The tube is held in a sulphuric-acid bath by a clamp. It should be short enough to allow a ready escape of the water formed, without danger of the contents frothing over the top. As heat is applied to the bath, the contents of the tube melt to a colorless liquid, which grows pink as the temperature rises and finally becomes dark red at 150°, at which point it becomes opaque, and a rapid giving off of water begins. More heat is applied, until the thermometer used in stirring the contents of the tube indicates 170°, at which point the reaction goes on most satisfactorily. After several hours the mass takes on a green luster, and the thermometer leaves marks on the sides of the tube, as though from

[1] White: Dissertation, 1891.

the crushing of some crystalline body. Careful examination, however, failed to reveal crystals, and the marks presently disappear. The evolution of water slackens as the mass grows viscous, and after heating for fifteen hours the contents of the tube are nearly solid. The thermometer is then taken out and the tube allowed to cool, when the contents usually break loose and can be readily removed.

When the reaction has proceeded properly the product is a black, resinous solid showing a green luster. It was powdered and washed with hot water to remove any phenol and ortho-sulpho-para-toluic acid remaining. Next it was dissolved in caustic potash, precipitated from its hot solution with hydrochloric acid, and washed with hot water until no test for chlorine was obtained with silver nitrate. The precipitate becomes more compact on boiling with water. It was dried by long standing in a desiccator.

Analogy with phenol-phthaleïn would lead to the supposition that a similar compound had been formed, having this structure:



The results of the analyses are in accordance with this supposition.

I. 0.5552 gram substance gave 0.3207 gram $BaSO_4$.

II. 0.2080 gram substance gave 0.1197 gram $BaSO_4$.

III. 0.1790 gram substance gave 0.0809 gram $H_2O$ and 0.3724 gram $CO_2$.

IV. 0.1992 gram substance gave 0.0881 gram $H_2O$ and 0.4154 gram $CO_2$.

| | Calculated for $C_{20}H_{14}O_5S + 3H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| C | 56.87 | ... | ... | 56.75 | 56.88 |
| H | 5.21 | ... | ... | 5.02 | 4.91 |
| S | 7.59 | 7.94 | 7.91 | ... | ... |

An attempt was made to determine the water given off on heating, but when a loss had taken place closely approximating that required by the above formula, traces of hydrogen sulphide were given off and the attempt was abandoned. This phenomenon has been noted by White in his investigation of sulphon-fluoresceïn.[1]

[1] Dissertation, 1891.

Pure di-phenol-para-methyl-sulphon-phthaleïn is not always obtained by the process just described, and an attempt to purify a mixed product was made, based on the solubility in water. After thorough washing the substances were treated with large quantities of boiling water; the hot filtered solution was evaporated to dryness on the water-bath, and a product was obtained having the same properties as the pure di-phenol derivative. Analysis showed their identity, except that the product last obtained contained less water, as might be expected from its manner of preparation.

I. 0.2641 gram substance gave 0.1126 gram $H_2O$ and 0.5854 gram $CO_2$.

II. 0.4167 gram substance gave 0.2540 gram $BaSO_4$.

| | Calculated for $C_{20}H_{14}O_6S + 1\frac{1}{2}H_2O$. | Found. I. | II. |
|---|---|---|---|
| C | 60.75 | 60.45 | ... |
| H | 4.81 | 4.74 | ... |
| S | 8.10 | ... | 8.37 |

Phenol-para-methyl-sulphon-phthaleïn is a dark-red, amorphous powder, slightly soluble in alcohol, ether and chloroform, and in warm glacial acetic acid. When these solvents are heated, a larger quantity dissolves, which on cooling comes down as a flaky precipitate. In alkaline carbonates, more readily in caustic alkalies, it dissolves to a red liquid much like an alkaline solution of phenol-phthaleïn. It shows a striking purple-red in dilute solution, which changes to yellow on the addition of acids. The purple color is not affected by exposure to the air, even for a long time.

All attempts to obtain a crystalline product by the use of the ordinary solvents were failures, but the use of a solution in water containing a little phenol was attended with better success. A clear, filtered solution was obtained, and, as nothing was deposited, the vessel containing it was covered with a watch-glass and allowed to stand in a sheltered place for several weeks. After some time, examination showed the presence of groups of short, yellow prisms floating from the surface of the liquid. Further evaporation caused these groups to grow, though the crystals always remained very small. When exposed to the air they took on a green luster. Their crystal character was not examined, as it was impossible to keep them without change after their removal from

the solution. The amount was too small for complete analysis. So far as is known, this is the only case of a crystalline sulphon-phthaleïn yet noted.

*Action of bromine on phenol-para-methyl-sulphon-phthaleïn.*—The substance was treated with the theoretical amount of bromine required to form a di-brom substitution-product. The bromine was used as a twenty-per cent. solution in glacial acetic acid, and was poured upon the sulphon-phthaleïn suspended in glacial acetic acid in a small Erlenmeyer flask. Reaction took place at once, accompanied by the production of heat and the evolution of hydrobromic acid. After standing a short time the whole was heated for half an hour on the water-bath and filtered through glass-wool. A small residue of unchanged phthaleïn was left on the filter. As the addition of water failed to produce any considerable precipitate, the solution was evaporated to dryness on the water-bath, and the residue was powdered and placed in a desiccator over caustic potash. The product thus obtained was a light brown powder, soluble to a considerable extent in water. In alkalies it dissolves with a deep-blue color, appearing greenish when dilute. The solution stains the skin a persistent blue which acids change to yellow. A determination of bromine gave the following result:

| | Calculated for $C_{20}H_{14}Br_2O_5S$. | Calculated for $C_{20}H_{12}Br_4O_5S$. | Found. |
|---|---|---|---|
| Br | 32.32 | 39.59 | 35.99 |

A second preparation was analyzed for bromine and sulphur.

I. 0.2152 gram substance gave 0.1954 gram AgBr.

II. 0.2400 gram substance gave 0.0801 gram $BaSO_4$.

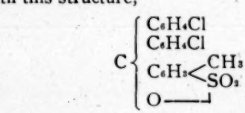
| | Calculated for $C_{20}H_{12}Br_4O_5S$. | Found. | |
|---|---|---|---|
| | | | II. |
| Br | 39.59 | 38.64 | ... |
| S | 5.29 | ... | 4.59 |

It seems, then, that a tri-brom substitution-product is formed; but, owing to the difficulty of separating it from the unchanged phthaleïn and from other substitution-products, it was not obtained in a perfectly pure form. Treatment with other proportions of bromine gave similar impure tri-brom derivatives.

*Action of phosphorus pentachloride on phenol-para-methyl-sulphon-phthaleïn.*—When this substance is treated in a small Erlenmeyer flask with a small excess of phosphorus pentachloride,

slight reaction takes place at once, and the mass becomes somewhat coherent, but after this first action nothing further takes place. Accordingly the flask was heated to 130° in a sulphuric-acid bath, when the mass melted and a lively effervescence followed. The heating was continued until all action had ceased. The product was a dark-red, viscous mass that when treated with water fell to an insoluble pink powder.

The most natural expectation would be that a product had been obtained with this structure,



The substance obtained, however, does not exhibit the properties of such a compound. It does not go into solution even when boiled with strong caustic potash, but is apparently subjected to a deeper decomposition, forming a turbid liquid with the potash, and giving off a phenol-like odor. Analysis of a specimen gave results that could not be readily interpreted, and, considering the properties of the substance, it is doubtful whether it was pure.

When ortho-sulpho-para-toluic acid is heated with four and with six molecules of phenol, products are obtained that appear to contain four and six residues of phenol respectively. The evidence as to their composition is, however, not conclusive.

### *Action of Pyrocatechin.*

To make a pyrocatechin-sulphon-phthaleïn, one equivalent of ortho-sulpho-para-toluic acid was heated with two equivalents of pyrocatechin in the usual way. Vigorous reaction took place, accompanied by a copious evolution of water, and the whole mass soon became viscous and clung to the sides of the tube. After two hours of heating at a temperature of 165° the reaction was completed, the substance being a black, friable mass. With water it became gelatinous and entirely prevented filtration. It was accordingly evaporated to dryness and powdered, when it still presented some of the same difficulties; but the washing was finally accomplished with a considerable loss of substance. Analysis showed surprising results.

I. 0.1000 gram substance gave 0.0203 gram $BaSO_4$.

II. 0.1280 gram substance gave 0.0246 gram $BaSO_4$.

III. 0.1172 gram substance gave 0.0468 gram $H_2O$ and 0.2897 gram $CO_2$.

IV. 0.1477 gram substance gave 0.0632 gram $H_2O$ and 0.3569 gram $CO_2$.

| | Calculated for $C_{30}H_{18}O_7S$. (2 mol. pyrocatechin.) | Calculated for $C_{44}H_{30}O_{10}S+2H_2O$. (6 mol.) | Calculated for $C_{56}H_{38}O_{13}S+3\frac{1}{2}H_2O$. (8 mol.) | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|---|---|
| C | 60.00 | 67.17 | 67.40 | .. | .. | 67.42 | 67.20 |
| H | 4.00 | 4.32 | 4.51 | .. | .. | 4.44 | 4.75 |
| S | 8.00 | 4.07 | 3.21 | 2.79 | 2.73 | .. | .. |

The results of analysis seem to agree best with the requirements of a compound containg *eight* residues of pyrocatechin. Though the percentages of carbon and hydrogen agree nearly as well for a hexa-pyrocatechin derivative, the percentages of sulphur are much nearer the requirements of the former compound. This formation of an octo-derivative would not be an isolated case; a similar compound of resorcinol will presently be described, and its character can be better discussed then. But it is unexpected that such a compound should be formed with the proportions used. It is to be regretted that the loss involved in its preparation left so little of the substance that its more detailed study was impossible. The compound is a black powder, dissolving in alkalies with an evanescent, grass-green color.

### *Action of Resorcinol.*

According to Fahlberg and Barge,[1] when ortho-sulpho-benzoic acid and resorcinol are heated in the molecular proportions of one to two or one to four, a condensation-product is obtained containing four resorcinol residues. White found that when the proportion of one to two was used a tetra-product resulted; but that when the proportions of one to four or one to six were used, a product was obtained containing six resorcinol residues, the conclusion being supported by analyses of a number of specimens. A series of three resorcinol-sulphon-phthaleïns was thus obtained.

The resorcinol-phthaleïns of ortho-sulpho-para-toluic acid have been treated by Jones.[2] Para-methyl-sulphon-fluoresceïn was made by heating para-methyl-dioxy-benzoyl-benzene-sulphonic acid, and chlorine and bromine compounds were obtained similar to those obtained with sulphon-fluoresceïn. It was also found

[1] Ber. d. chem. Ges. **22**, 765.

[2] Dissertation, 1891.

that heating together resorcinol and ortho-sulpho-para-toluic acid in the proportion of two to one gave a tetra-resorcinol product, while the use of the proportions four to one and six to one gave a compound containing six residues of resorcinol. A series of three methyl-sulphon-phthaleïns was thus obtained. As it seemed desirable to investigate these latter compounds further, the following work was done.

*Treatment of ortho-sulpho-para-toluic acid with various proportions of resorcinol.*—One molecule of ortho-sulpho-para-toluic acid was heated with two molecules of resorcinol. The resorcinol melted and dissolved the acid, forming a red liquid. Reaction began at 150°, and the mass was allowed to remain at 170° for about two hours. It gradually grew stiff, and on cooling was a brittle, black solid, giving a dark-red powder. It was purified in the usual way. In water it dissolved slightly with a yellow color, and with alkalies it gave the characteristic red-green fluorescence. A determination of sulphur was made.

| | Calculated for $C_{28}H_{14}O_8S+H_2O$. (2 mol.) | Calculated for $C_{35}H_{22}O_8S+3H_2O$. (4 mol.) | Found. I. | Found. II. |
|---|---|---|---|---|
| S | 8.39 | 5.17 | 6.16 | 5.86 |

The results indicate that a tetra-resorcinol derivative had been obtained.

When ortho-sulpho-para-toluic acid and resorcinol in the proportion of one to four were heated together, reaction was completed in about two hours, the product being an exceedingly brittle, black substance having properties similar to those of the substance just described. Determinations of sulphur in the washed product were made.

I. 0.2028 gram substance gave 0.0634 gram $BaSO_4$.

II. 0.3122 gram substance gave 0.0973 gram $BaSO_4$.

| | Calculated for $C_{44}H_{30}O_{16}S.4H_2O$. | Calculated for $C_{44}H_{30}O_{16}S.3H_2O$. | Found. I. | Found. II. |
|---|---|---|---|---|
| S | 3.90 | 3.98 | 4.30 | 4.28 |

A fairly pure hexa-resorcinol derivative was obtained; but the substance was obtained in a better form by the use of other proportions.

*Hexa-resorcinol-para-methyl-sulphon-phthaleïn.* — Ortho-sulpho-para-toluic acid and resorcinol in the molecular proportions of one to six were heated in a short tube. At 150° vigorous reac-

tion began, and the temperature was allowed to rise very slowly with constant stirring by the thermometer until 170° was indicated. At the end of five hours the almost solid mass was allowed to cool. It was, like the other resorcinol compounds, a brittle, black mass showing electrical properties when rubbed. When powdered and placed in water, it softens and then grows hard again, forming small porous grains. It was twice dissolved in caustic potash, precipitated with hydrochloric acid and washed on the filter.

The product is a dark-red powder rather difficult to handle when dry, as it becomes electrified when stirred. It dissolves in water to a slight extent, giving a light-yellow solution with a tendency to fluorescence. When boiled with water it becomes more compact. It dissolves at once in alkalies, less readily in alkaline carbonates, giving a red solution showing a strong green fluorescence. When diluted it shows a pink-green fluorescence. On standing in alkaline solution for several days, a slight reddish precipitate settles and the color of the solution becomes less intense. Zinc dust and caustic potash reduce it to a yellow solution; this when filtered from the zinc dust quickly oxidizes again. It is slightly soluble in alcohol and ether, and in warm glacial acetic acid. Hot water containing resorcinol dissolves a considerable quantity, which on cooling separates as an impalpable powder, rendering the liquid turbid. Attempts to crystallize the substance were unsuccessful.

The results of analysis are as follows:

I. 0.2928 gram substance gave 0.0830 gram $BaSO_4$.

II. 0.2197 gram substance gave 0.0622 gram $BaSO_4$.

III. 0.1507 gram substance gave 0.0640 gram $H_2O$ and 0.3623 gram $CO_2$.

IV. 0.1668 gram substance gave 0.0703 gram $H_2O$ and 0.4011 gram $CO_2$.

| | Calculated for $C_{44}H_{30}O_{10}S.4H_2O$. (Jones). | Calculated for $C_{44}H_{30}O_{10}S.3H_2O$, or $C_{44}H_{36}O_{13}S$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|---|
| C | 64.21 | 65.67 | ... | ... | 65.56 | 65.59 |
| H | 4.63 | 4.48 | ... | .... | 4.71 | 4.67 |
| S | 3.90 | 3.98 | 3.90 | 3.89 | ... | ... |

Whether the three molecules of so-called water exist as such or as hydroxyl groups in the resorcinol residues, could not be deter-

mined. Attempts to drive off the water by heating were unsuccessful, the substance melting at 200° before a loss corresponding to three molecules of water had occurred. No trace of hydrogen sulphide was detected.

*Action of eight molecules of resorcinol on ortho-sulpho-para-toluic acid.*—Ortho-sulpho-para-toluic acid and resorcinol, one equivalent of the former to eight of the latter, were heated in the usual manner in a sulphuric-acid bath. Reaction took place readily, about ten hours being required for its completion. At the end of that time the mass had become too stiff to be stirred with the thermometer, and was accordingly allowed to cool, when it broke loose from the sides of the tube and could be obtained in the form of a stick. When rubbed it exhibited electrical properties, and when powdered and thrown upon water it at first softened and then hardened to a friable mass. When the stick was broken it showed a radiating structure, with curved surfaces. It was powdered and washed with warm water and then twice dissolved in alkali and reprecipitated with hydrochloric acid, being each time filtered and washed. It was finally dried for a long time in a desiccator. Two determinations of sulphur were made.

I. 0.2485 gram substance gave 0.0594 gram $BaSO_4$.

II. 0.2836 gram substance gave 0.0658 gram $BaSO_4$.

| | Calculated for $C_{44}H_{38}O_{13}S$. (6 mol. resorcinol.) | Calculated for $C_{52}H_{46}O_{14}S$. (8 mol. resorcinol.) | Found. I. | Found. II. |
|---|---|---|---|---|
| S | 3.98 | 3.18 | 3.29 | 3.19 |

As only a small quantity of the compound had been made, a complete analysis was not attempted; accordingly a second preparation was made, using larger quantities. This product was in every way similar to the one first obtained.

I. 0.1727 gram substance gave 0.0696 gram $H_2O$ and 0.4238 gram $CO_2$.

II. 0.1660 gram substance gave 0.0677 gram $H_2O$ and 0.4065 gram $CO_2$.

III. 0.1547 gram substance gave 0.0628 gram $H_2O$ and 0.3805 gram $CO_2$.

IV. 0.1298 gram substance gave 0.0524 gram $H_2O$ and 0.3174 gram $CO_2$.

V. 0.2197 gram substance gave 0.0495 gram $BaSO_4$.

| | Calculated for $C_{88}H_{46}O_{16}S$. | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| C | 66.80 | 66.86 | 66.75 | 67.07 | 66.69 | ... |
| H | 4.57 | 4.48 | 4.53 | 4.52 | 4.49 | ... |
| S | 3.18 | ... | ... | ... | ... | 3.10 |

A third product, similar to the other two, was made and analyzed.

I. 0.1543 gram substance gave 0.0625 gram $H_2O$ and 0.3774 gram $CO_2$.

II. 0.2426 gram substance gave 0.0570 gram $BaSO_4$.

III. 0.2629 gram substance gave 0.0626 gram $BaSO_4$.

| | Calculated for $C_{88}H_{46}O_{16}S$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 66.80 | 66.71 | ... | ... |
| H | 4.57 | 4.50 | ... | ... |
| S | 3.18 | ... | 3.23 | 3.27 |

The following is the average of all the determinations made, compared with the composition of various phthaleïns.

| | Average Found. | $C_{88}H_{46}O_{16}S$. (8 mol.) | $C_{44}H_{26}O_{13}S.3H_2O$. (6 mol.) | $C_{44}H_{30}O_{15}S.2H_2O$. (6 mol.) |
|---|---|---|---|---|
| C | 66.81 | 66.80 | 65.67 | 67.17 |
| H | 4.50 | 4.57 | 4.48 | 4.32 |
| S | 3.21 | 3.18 | 3.98 | 4.07 |

While the evidence in favor of the formula $C_{88}H_{46}O_{16}S$ is, therefore, strong, it seems nevertheless premature to speculate in regard to the structure of this curious product.

*Action of bromine on octo-resorcinol-para-methyl-sulphon-phthaleïn.*—Two grams of the phthaleïn were treated in a small Erlenmeyer flask with a large excess of bromine in the form of a twenty-per cent. solution in glacial acetic acid. Heat was at once developed. After about one hour's gentle heating on the water-bath, with the occasional addition of bromine, solution had taken place, giving a dark-red liquid, from which, on cooling, amorphous crusts were deposited. The addition of water threw down a pink, finely-divided precipitate, very hard to wash. The heated liquid was accordingly made alkaline with caustic potash, and the substance in solution was precipitated by hydrochloric acid as a red precipitate resembling ferric hydroxide. A determination of bromine gave Br: 47.60. A substituted octo-resorcinol-para-methyl-sulphon-phthaleïn of the formula $C_{56}H_{38}Br_{11}O_{16}S$ would give 46.8 per cent. of bromine.

A further endeavor to obtain a pure product was made. The same process was followed, the heating on the water-bath being succeeded by heating in a sulphuric-acid bath to the boiling-point of the acetic acid. A compound similar to the first was formed, which gave the following results on analysis:

I. 0.1540 gram substance gave 0.0295 gram $H_2O$ and 0.1943 gram $CO_2$.

II. 0.2171 gram substance gave 0.2507 gram AgBr.

| | Calculated for $C_{24}H_{24}Br_{12}O_{18}S$. | Found. I. | II. |
|---|---|---|---|
| C | 34.44 | 34.42 | ... |
| H | 1.74 | 2.13 | ... |
| Br | 49.00 | ... | 49.14 |

It seems that bromine readily enters the compound at first, but that this action takes place less readily as more and more enters, until prolonged action is needed to force the eleventh and twelfth atoms into combination. These substances are very similar to eosin in their properties. They dissolve readily in alkalies, giving a deep-red color when concentrated. When diluted the solution shows the delicate fluorescence of tetra-brom-fluorescein.

### *Action of Orcinol.*

The action of orcinol upon ortho-sulpho-benzoic acid has been investigated by Mr. J. E. Gilpin, the results being published in his dissertation (1892). He obtained a di-orcinol and a tetra-orcinol derivative of the acid, orcinol showing less readiness than resorcinol to enter into combination.

One equivalent of ortho-sulpho-para-toluic acid was heated with two equivalents of orcinol. The orcinol melted and dissolved the acid, but reaction was somewhat slow in taking place, being completed only after ten hours' heating at 170°. The resulting solid mass was powdered and washed with hot water, with which it does not become gummy. It was then treated in the usual manner.

I. 0.1774 gram substance gave 0.0734 gram $H_2O$ and 0.4197 gram $CO_2$.

II. 0.1747 gram substance gave 0.0744 gram $H_2O$ and 0.4118 gram $CO_2$.

III. 0.2068 gram substance gave 0.1100 gram $BaSO_4$.

| | Calculated for $C_{25}H_{18}O_6S$. (2 mol. orcinol.) | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 64.39 | 64.52 | 64.28 | ... |
| H | 4.39 | 4.60 | 4.73 | ... |
| S | 7.80 | ... | ... | 7.31 |

The substance seems to be a di-orcinol derivative containing, perhaps, a little of a higher phthalein from which it could not well be separated. It is a bright-red powder, dissolving in alkalies with a red color, and showing a green fluorescence considerably weaker than that of resorcinol phthaleïns.

*Action of Hydroquinone.*

Reaction between hydroquinone and ortho-sulpho-para-toluic acid does not readily take place, a compound being formed only after long-continued heating. When the two substances in the molecular proportion of two to one were heated in the usual manner a clear liquid was formed at 170°. At a temperature of 185° slight coloration began, accompanied by a gradual evolution of water. After about fifty hours an opaque viscous mass resulted, which on cooling formed a brittle, black solid. It was purified in the usual manner, and analyzed with the following result:

I. 0.1643 gram substance gave 0.0586 gram $BaSO_4$.

II. 0.1676 gram substance gave 0.0601 gram $BaSO_4$.

III. 0.1750 gram substance gave 0.0670 gram $BaSO_4$.

IV. 0.1617 gram substance gave 0.0582 gram $H_2O$ and 0.3928 gram $CO_2$.

V. 0.1624 gram substance gave 0.0577 gram $H_2O$ and 0.3935 gram $CO_2$.

| | Calculated for $C_{20}H_{14}O_6S$. (2 mol. hydroquinone.) | Calculated for $C_{32}H_{24}O_8S.H_2O$. (4 mol. hydroquinone.) | I. | II. | Found. III. | IV. | V. |
|---|---|---|---|---|---|---|---|
| C | 63.09 | 65.75 | ... | ... | ... | 66.25 | 66.17 |
| H | 3.66 | 4.12 | ... | ... | ... | 4.00 | 3.95 |
| S | 8.38 | 5.47 | 4.90 | 4.93 | 5.26 | ... | ... |

It thus appears that a di-hydroquinone product is not formed, but, instead, one containing four residues of the phenol.

Tetra-hydroquinone-para-methyl-sulphon-phthaleïn is a compact brown powder soluble in a large quantity of water with a yellow color. In alkalies it readily dissolves with a red color. Zinc dust and caustic potash reduce it to a nearly colorless substance.

### *Action of Pyrogallol.*

An experiment is described by White,[1] in which, on heating together pyrogallol and ortho-sulpho-benzoic acid, he obtained a substance having properties like those of galleïn; the compound was not analyzed. Attempts, described below, to obtain a methyl-sulphon-analogue of galleïn were successful, resulting in the formation of at least two phthaleïns.

*Para-methyl-sulphon-galleïn.*—This compound was formed by heating together ortho-sulpho-para-toluic acid and pyrogallol in the molecular proportion of one to two. The clear liquid formed when these melted grew darker, and at 160° vigorous reaction took place; to prevent the fused mass from rising to the mouth of the tube, continuous stirring was necessary. After two hours' heating, the product was a stiff substance that clung to the sides of the tube. On cooling, it formed a brittle mass that when exposed to the air for any length of time became sticky. Accordingly it was quickly powdered and mixed with water, when it dissolved to a large extent, giving a brown solution. Attempts to filter off the undissolved substance being unsuccessful, as the paper became packed with the gelatinous mass, the liquid was treated with caustic potash, and then acidified with hydrochloric acid, but attempts to filter met with no better success. The acidified liquid was then evaporated to dryness on the water-bath and the residue powdered. It now presented more agreeable characteristics: it did not become sticky in the air, and, though still rather easily soluble in water, the part not dissolved sank to the bottom of the beaker and was easily filtered off and washed. The dried product gave the following analytical results:

I. 0.1298 gram substance gave 0.0435 gram $H_2O$ and 0.2649 gram $CO_2$.

II. 0.1274 gram substance gave 0.0426 gram $H_2O$ and 0.2605 gram $CO_2$.

III. 0.1588 gram substance gave 0.0820 gram $BaSO_4$ (Liebig).

IV. 0.1477 gram substance gave 0.0749 gram $BaSO_4$ (Liebig).

V. 0.1361 gram substance gave 0.0701 gram $BaSO_4$ (Liebig).

| | Calculated for $C_{20}H_{14}O_8S$. (*p*-methyl-sulphon-galleïn). | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| C | 55.55 | 55.67 | 55.76 | ... | ... | ... |
| H | 3.70 | 3.72 | 3.72 | ... | ... | ... |
| S | 7.40 | ... | ... | 7.10 | 7.03 | 7.08 |

[1] Dissertation, 1891.

The fact that the percentages of carbon are high, while sulphur comes persistently low, would indicate that the substance analyzed may have contained a small quantity of a higher phthaleïn; this would cause the variation noted from the theoretical percentages.

Para-methyl-sulphon-galleïn is a blue-black powder, rather easily soluble in water, its dilute solution having a yellow color. If a drop of alkali is allowed to fall upon such a solution, a beautiful sky-blue color is produced. On stirring, and especially in more concentrated solutions, the blue is soon succeeded by a rich purple, often so deep as to appear black. An excess of acid brings back a yellowish-brown color, but the precipitate formed will not settle. When allowed to stand in the air, the alkaline solution gradually fades and becomes almost colorless, and a brown substance is deposited. The addition of a little stannous chloride makes the blue color more persistent.

*Hexa-pyrogallol-para-methyl-sulphon-galleïn.*—One equivalent of ortho-sulpho-para-toluic acid was heated with four equivalents of pyrogallol. Reaction was even more vigorous than in the preceding case, and after an hour's heating at 160° a solid mass resulted. On cooling it was brittle, black and quickly became sticky. It presented in an exaggerated form the difficulties encountered in the purification of methyl-sulphon-galleïn, but after being evaporated to dryness it was filtered and washed, a considerable loss resulting from its solubility.

The most probable product from the reaction of the proportions used was a compound containing four residues of pyrogallol. If, however, the reaction should take place as with resorcinol, a substance containing six such residues might be expected. Analysis showed that the latter was the case.

I. 0.1812 gram substance gave 0.0644 gram $H_2O$ and 0.4001 gram $CO_2$.

II. 0.1740 gram substance gave 0.0615 gram $H_2O$ and 0.3850 gram $CO_2$.

III. 0.2340 gram substance gave 0.0639 gram $BaSO_4$.

IV. 0.3566 gram substance gave 0.0995 gram $BaSO_4$.

| | Calculated for $C_{33}H_{22}O_{12}S$. (4 mol. pyrogallol.) | Calculated for $C_{44}H_{26}O_{18}S.1\frac{1}{2}H_2O$. (6 mol.) | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|---|
| C | 60.90 | 60.47 | 60.22 | 60.34 | ... | ... |
| H | 3.49 | 3.78 | 3.94 | 3.92 | ... | ... |
| S | 5.08 | | ... | ... | 3.75 | 3.83 |

Hexa-pyrogallol-para-methyl-sulphon-phthaleïn is a black powder rather easily soluble in water, and giving a rose color when such a solution is diluted. A drop of alkali causes a beautiful, evanescent sky-blue color. If some stannous chloride is added to a water solution of the phthaleïn and the alkali is then added, the blue comes out beautifully and remains for some time. After the disappearance of the blue, a purple takes its place, slowly fading to a brown and finally to a yellow. After standing for a week, even in sealed tubes, all color disappears. Zinc and caustic potash give a yellow solution.

With most of the phthaleïns described, attempts were made by treatment with bromine, with acetic anhydride, and with phosphorus pentachloride to get definite products, in the hope of throwing light upon the nature of the phthaleïns, but these attempts did not lead to satisfactory results.

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## IV.—ORCIN-SULPHON-PHTHALEÏN.

By J. E. Gilpin.

Orcin and ortho-sulpho-benzoic acid (2 molecules of the orcin to 1 of the acid) were well mixed and put in a short tube which was suspended in a sulphuric-acid bath. A thermometer was used as a stirring-rod in order that the temperature might be easily regulated. The temperature was slowly raised to 80°, at which point the orcin melted to a straw-yellow colored liquid. The acid dissolved in this as the temperature rose, and at 160°–170° water began to come off. Constant stirring, especially in the early stages of the action, is necessary, as in many cases it would not be complete without it. The color gradually turned to dark red, and after the mass had become slightly stiff it was heated to 180° until it was too stiff to stir. If the tube is plunged into cold water while still warm, the material on cooling suddenly breaks away from the glass and can be extracted without difficulty. After being powdered it was washed well with the aid of the filter-pump, to remove any excess of the orcin or acid, and then dissolved in alkali. The substance is obtained from this solution by adding hydrochloric acid, when it is precipitated as a flocculent mass. It was found much easier to wash this precipitate if the liquid was first evaporated

off and the mixture of the compound and sodium chloride well powdered. This was washed until the sodium chloride was removed and the wash-water showed no marked color, then dried on porous plates and drying-paper. The powder prepared in this way is of a dark-red color, easily soluble in alkali, with a marked red and green fluorescence; nearly insoluble in water, and slightly soluble in alcohol and ether. On evaporating the solutions, however, it always comes down as a powder and shows no tendency to crystallize. Four specimens were made in this way, using the same proportions; but only one of these was approximately pure. The general tendency seem to be towards the formation of the di- and tetra-products mixed, whether the orcin is present in the proportions of two or four molecules. Fischer,[1] in his work on the action of orcin on phthalic-acid anhydride, found that one of the oxygen atoms was replaced by two orcin residues, water being eliminated in the reaction.

It was expected that with the ortho-sulpho-benzoic acid a similar action would take place, leading to the formation of a diorcin derivative of ortho-sulpho-benzoic acid. From the work on this product it can hardly be doubted that diorcin-sulphon-phthaleïn is formed; but generally there is some tetraorcin-sulphon-phthaleïn formed at the same time. As Baeyer showed that in the action of resorcin on phthalic anhydride it was not the anhydride oxygen which was replaced but one of the others, we should expect the same to hold good here.

*Preparation I.*

0.131 gram of the substance gave 0.0698 gram $BaSO_4$ (Liebig).

0.1752 gram of the substance gave 0.0707 gram $H_2O$ and 0.3875 gram $CO_2$.

*Preparation II.*

0.1376 gram of the substance gave 0.0692 gram $BaSO_4$.

0.1305 gram of the substance gave 0.0613 gram $BaSO_4$.

0.1411 gram of the substance gave 0.0686 gram $BaSO_4$.

0.1009 gram of the substance gave 0.0475 gram $BaSO_4$.

0.1682 gram of the substance gave 0.0693 gram $H_2O$ and 0.3730 gram $CO_2$.

0.2992 gram of the substance gave 0.1184 gram $H_2O$ and 0.6725 gram $CO_2$.

[1] Ber. d. chem. Ges. 7, 1214.

*Preparation III.*

0.1826 gram of the substance gave 0.1048 gram $BaSO_4$.

0.1451 gram of the substance gave 0.0634 gram $H_2O$ and 0.3340 gram $CO_2$.

0.1703 gram of the substance gave 0.0715 gram $H_2O$ and 0.3921 gram $CO_2$.

*Preparation IV.*

0.1128 gram of the substance gave 0.0571 gram $BaSO_4$.

| | Calculated for $C_{21}H_{18}O_7S$. | Found. I. | II. | | | | III. | | IV. |
|---|---|---|---|---|---|---|---|---|---|
| C | 60.86 | 60.31 | 60.47 | 61.29 | ... | ... | 62.77 | 62.78 | ... |
| H | 4.34 | 4.48 | 4.57 | 4.43 | ... | ... | 4.82 | 4.66 | ... |
| S | 7.72 | 7.32 | 6.91 | 6.45 | 6.68 | 6.46 | 7.88 | ... | 6.95 |

The first of these was comparatively pure diorcin-sulphon-phthaleïn. The others, however, contained amounts of carbon and sulphur which would correspond to mixtures of the di- and tetraorcin-sulphon-phthaleïn, varying according to the proportions of each present, but in general showing a greater tendency towards the tetraorcin-sulphon-phthaleïn. From this it was thought that a pure tetra-product could be obtained by the use of more orcin in proportion to the acid, but it was found that this was not the case.

Experiment showed that when the acid is heated with orcin in the proper proportions an approximately pure tetra-product was formed, but it could not be obtained in pure condition.

## ON PARA-CHLOR-META-SULPHO-BENZOIC ACID AND SOME OF ITS DERIVATIVES.[1]

By H. M. Ullmann.

*Para-chlor-benzoic acid from commercial saccharin.*—My attention was directed to *p*-chlor-benzoic acid by observing its

[1] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1892.

occurrence in commercial saccharin. In the preparation of *o*-sulpho-benzoic acid from the benzoic sulphinide contained in saccharin, the latter substance is boiled for several hours with dilute hydrochloric acid in a flask connected with a reflux condenser; the benzoic sulphinide is thus converted into the acid ammonium salt of *o*-sulpho-benzoic acid, which is soluble in water; the *p*-sulphamine-benzoic acid originally contained in the saccharin remains unchanged and is insoluble in cold water.[1] During this operation there is frequently formed a volatile product which condenses in white flocculent masses and is returned with condensed water-vapor, and is insoluble in cold water. After the operation has been completed the contents of the flask are allowed to cool; the soluble acid ammonium salt of *o*-sulpho-benzoic acid is filtered off. The volatile white flocculent substance, which proved to be *p*-chlor-benzoic acid, can be recovered from the insoluble residues by distillation with steam, whereby it passes over and can be collected in almost pure condition. It is very difficultly soluble in cold water, and can be purified without loss by dissolving it in a solution of sodium carbonate and reprecipitating with sulphuric acid. It can be distilled with steam directly out of saccharin by the addition of a mineral acid to the saccharin. Para-chlor-benzoic acid is therefore in all probability present in saccharin in the form of a salt, and is freed from the base by the addition of the mineral acid. From one specimen of saccharin no *p*-chlor-benzoic acid could be obtained.

In the methods of analysis hitherto devised for the determination of the benzoic sulphinide and the impurities contained in saccharin, the presence of *p*-chlor-benzoic acid as an impurity has not been regarded. According to the method of Remsen and Burton,[2] which is based on the quantitative conversion of the sulphinide into the acid ammonium salt of *o*-sulpho-benzoic acid, the *p*-chlor-benzoic acid is freed from its base and is estimated along with the *p*-sulphamine-benzoic acid as an impurity. If it were desired to make a special determination of the *p*-chlor-benzoic acid, it would only be necessary to modify this method by distilling the *p*-chlor-benzoic acid off from the *p*-sulphamine-benzoic acid and weighing each separately.

In the method of Salkowski no acid is used; the *p*-chlor-benzoic acid remains combined with its base as a soluble salt and is

[1] Remsen and Dohme: This Journal **11**, 332. [2] This Journal **11**, 403.

estimated, along with all substances which are more soluble than *p*-sulphamine-benzoic acid, as benzoic sulphinide.

The presence of a salt of *p*-chlor-benzoic acid will explain the occurrence of chlorine in the ash of saccharin pointed out by S. Hirschfeld.[1]

The volatility with water-vapor of *p*-chlor-benzoic acid has not hitherto been recorded. The *m*-chlor-benzoic acid and the *o*-chlor-benzoic acid are not volatile with water-vapor. Beilstein and Kuhlberg[2] found that the di-chlor-benzoic acid in which one of the chlorine atoms is in the para position relative to the carboxyl group, is volatile with water-vapor. As far as these observations go, it would seem that the volatility with water-vapor of chlor-substitution-products of benzoic acid is in some way dependent on the para position of the chlorine.

The *p*-chlor-benzoic acid obtained from commercial saccharin agreed in all respects with the descriptions given by Beilstein and Geitner,[3] and by Emmerling,[4] and with *p*-chlor-benzoic acid which I prepared later on from *p*-chlor-toluene. It is precipitated by acids from its soluble sodium salt in white flocculent masses, and sublimes in needles which melt at 234°. The calcium salt crystallizes in arborescent forms with three molecules of water of crystallization. Analyses of the calcium salt resulted as follows:

I. 0.2584 gram salt gave 0.0874 gram $CaSO_4$ = 0.0252 gram Ca.

II. 0.2189 gram salt gave 0.0730 gram $CaSO_4$ = 0.0215 gram Ca.

| | Calculated for $(C_6H_4ClCOO)_2Ca+3H_2O$. | Found. I. | II. |
|---|---|---|---|
| Ca | 9.88 | 9.92 | 9.81 |

The identity of the *p*-chlor-benzoic acid obtained from commercial saccharin was thus fully confirmed.

[1] Thesis: Ein Beitrag zur Saccharinfrage. Erlangen, 1891.

Hirschfeld has again used the empirical method devised by Salkowski for the analysis of saccharin after so exact a method as that of Remsen and Burton has been devised. I have had occasion to prepare pure benzoic sulphinide from commercial saccharin, and from personal experience and the experience of many others I know that no reliance whatever is to be placed on the method of Salkowski, which depends on the suppositions that benzoic sulphinide and *p*-sulphamine-benzoic acid can be separated by three fractional crystallizations in water, and that the resulting mother-liquors upon evaporation give approximately pure benzoic sulphinide. Hirschfeld confirms the erroneous statement of Salkowski that benzoic sulphinide after long-continued boiling with dilute hydrochloric acid is left unchanged. Hirschfeld again confirms Salkowski's error in the melting-point of pure benzoic sulphinide, and gives it at 213°. It is 222°-223°. The various connections in which the name of Professor Ira Remsen is used in this thesis by Hirschfeld can be ascribed only to ignorance of the literature.

[2] Ann. Chem. (Liebig) **152**. [3] *Ibid.* **139**, 336. [4] Ber. d. chem. Ges. **8**, 880.

*Para-chlor-benzoic acid from p-sulphamine-benzoic acid.*—For a supply of *p*-chlor-benzoic acid to be utilized in a reinvestigation of its sulphonic-acid derivative, it was found necessary to use some other method of preparation than the distillation from commercial saccharin. It was thought that by treating *p*-sulphamine-benzoic acid with an excess of phosphorus pentachloride at a high temperature, the sulphonamide group would be driven out and replaced by chlorine. Then upon saponifying the resulting *p*-chlor-benzoyl chloride it would be transformed into *p*-chlor-benzoic acid, and could then be distilled with steam from the accompanying impurities. This reaction has been successful with many sulphonic acids; a case bearing directly on the experiment in question is the conversion of di-chlor-para-sulpho-benzoic acid into tri-chlor-benzoic acid accomplished by R. Otto.[1] In the case of a sulphamine-benzoic acid the action of phosphorus pentachloride might result in the formation of *p*-chlor-benzonitrile, analogous to the formation of *o*-chlor-benzonitrile from benzoic sulphinide and phosphorus pentachloride.[2] Both of these suppositions were realized, but the yield of *p*-chlor-benzoic acid was too small to recommend the use of this method as a practical one for the preparation of the acid in quantity.

*Para-chlor-benzoic acid from p-chlor-toluene.*—While the experiments described above were in progress, other experiments were being carried on with Emmerling's method for the preparation of *p*-chlor-benzoic acid.[3] By this method small quantities of *p*-chlor-toluene are treated with dilute solutions of potassium permanganate containing one part of permanganate to three parts of *p*-chlor-toluene used. Taking into account that ordinary *p*-chlor-toluene contains from twenty-five to fifty per cent. of *o*-chlor-toluene, and that for a complete decoloration of the dilute permanganate solution about nine hours are necessary, this method is not more rapid than the one above described for getting *p*-chlor-benzoic acid out of *p*-sulphamine-benzoic acid. But it was found that concentrated solutions of potassium permanganate with an excess of *p*-chlor-toluene yield satisfactory results. The following method is the best one available for the preparation of *p*-chlor-benzoic acid: Into a four-liter globe-flask containing three liters of distilled water are put one hundred and fifty grams of potassium

[1] Ann. Chem. (Liebig) **123**, 226. [2] Remsen and Dohme: This Journal **11**, 332.
[3] Ber. d. chem. Ges. **8**, 880.

permanganate. To this is added fifty to seventy cubic centimeters of *p*-chlor-toluene. The flask is placed in a bath of boiling water and is connected with a reflux condenser. After having been kept at the temperature of boiling water for twelve to fifteen hours the color of the permanganate disappears. The excess of *p*-chlor-toluene is readily recovered by distillation with steam. While still hot the soluble salts of para- and ortho-chlor-benzoic acid are filtered from the insoluble hydroxides of manganese. The solution of potassium para- and ortho-chlor-benzoate is allowed to cool and is then treated with sulphuric acid, whereby the *p*-chlor-benzoic acid is completely precipitated together with a little *o*-chlor-benzoic acid. The greater part of the *o*-chlor-benzoic acid remaining in solution is filtered from the insoluble portion. The *p*-chlor-benzoic acid is completely freed from *o*-chlor-benzoic acid by washing two or three times with a little hot water. The *o*-chlor-benzoic acid can be recovered in nearly pure condition from the filtrate by evaporating. It still contains a little *p*-chlor-benzoic acid, which is got rid of by distilling it out with steam, or more simply by repeatedly dampening the impure *o*-chlor-benzoic acid with water and placing it in an air-bath at 120°. After two or three such operations the *o*-chlor-benzoic acid is free from all *p*-chlor-benzoic acid.

The recovered excess of chlor-toluene is again treated as above. In thus treating the recovered excess of para- and ortho-chlor-toluene no marked change in the ratio of *p*-chlor-benzoic acid to *o*-chlor-benzoic acid obtained was observed, and it is probable that the oxidation of *p*-chlor-toluene and that of *o*-chlor-toluene by potassium permanganate take place with about the same rapidity.

*Para-chlor-meta-sulpho-benzoic acid.* — This acid has been investigated by Th. Cöllen and C. Böttinger.[1] They described methods of preparation from *p*-chlor-benzoic acid by treating it with sulphuric anhydride, or with fuming sulphuric acid containing ninety per cent. of sulphuric anhydride.

In attempts to determine the position of the sulphonic acid group they employed the following methods: Reduction of the free acid with sodium amalgam in the expectation of replacing the para-chlorine atom by hydrogen and thereby converting the acid into a known sulpho-benzoic acid; fusion of the potassium salt

[1] Ber. d. chem. Ges. **9**, 758, 1247.

with caustic potash and silver oxide in order to obtain a dihydroxy-benzoic acid; fusion of the potassium salt with sodium formate in the hope of obtaining mono-, di- and tri-carbonic acids of benzene. From these experiments no conclusion was reached as to the constitution of the acid, which will be shown to be *p*-chlor-*m*-sulpho-benzoic acid.

By treatment of the sodium salt with phosphorus pentachloride they prepared a mixture of chlorides to which the formula $C_6H_3\begin{cases}Cl\\COOH\\SO_2Cl\end{cases}$ and $C_6H_3\begin{cases}Cl\\COCl\\SO_3OH\end{cases}$ were ascribed. It will be shown that the di-chloride, $C_6H_3\begin{cases}Cl\\COCl,\\SO_2Cl\end{cases}$ is obtained by this reaction. By successive treatment of the sodium salt with phosphorus pentachloride and ammonia they obtained what was described as an amide-ammonium salt, and to which they gave the formula $C_6H_3Cl\overset{SO_3}{\underset{CO}{}}ONH_4, NH_2$. It will be shown that these reactions lead to the di-amide $C_6H_3\begin{cases}Cl\\CONH_2\\SO_2NH_2.\end{cases}$

Although Cöllen and Böttinger preferred to convert *p*-chlor-benzoic acid into its sulphonic-acid derivative by the use of fuming sulphuric acid containing ninety per cent. of sulphuric anhydride, I have found the reaction with sulphuric anhydride alone more satisfactory. An attempt to prepare the sulphonic-acid derivative by first converting the *p*-chlor-benzoic acid into *p*-chlor-benzoyl-chloride and then treating with fuming sulphuric acid, or with fuming sulphuric acid and sulphuric anhydride, was not as successful. After standing four days the mass still gave a precipitate of *p*-chlor-benzoic acid when boiled with water.

The method adopted as the most practicable is the following one: Into a receiver is placed dry powdered *p*-chlor-benzoic acid, and into it is distilled sulphuric anhydride from a retort containing fuming sulphuric acid. A brownish viscous mass is formed. By occasionally heating this mass to the boiling-point of the sulphuric anhydride, the reaction is hastened and is fully completed in the course of a day. The contents of the receiver are now transferred to a retort and the excess of sulphuric anhydride is distilled off. The *p*-chlor-sulpho-benzoic acid thus formed is

poured into water and dissolves completely. The solution is treated with barium carbonate, and the filtrate from the barium sulphate gives after concentration excellent crystals of barium *p*-chlor-*m*-sulpho-benzoate, difficultly soluble in cold water. The final mother-liquors from the crystallizations of the barium salt of *p*-chlor-*m*-sulpho-benzoic acid contained a much more soluble barium salt. This more soluble salt is not the salt of *p*-chlor-*o* sulpho-benzoic acid, as was found by comparing the free acid and some of its derivatives with the substances obtained by J. J. de Roode from *p*-chlor-toluene-*o*-sulphonic acid.[1] It is probably the barium salt of a *p*-chlor-di-sulpho-benzoic acid.

The acid obtained in free condition by exactly precipitating the barium in barium *p*-chlor-*m*-sulpho-benzoate with sulphuric acid, crystallized from water in long needles. It is very soluble in water. An analysis of the acid gave the following results:

I. 0.2671 gram acid heated to constant weight at 150° lost 0.0492 gram $H_2O$.

II. 0.1225 gram acid gave by Carius method 0.1004 gram $BaSO_4 = 0.0138$ gram S, and 0.0609 gram $AgCl = 0.0151$ gram Cl.

| Calculated for $C_6H_3\begin{cases}Cl\\SO_3H\\CO_2H\end{cases} + 3H_2O$. | | Found. |
|---|---|---|
| $H_2O$ | 18.59 | 18.42 |
| S | 11.04 | 11.24 |
| Cl | 12.21 | 12.29 |

The copper, sodium, potassium, lead and zinc salts were made and were found to agree with the descriptions given by Cöllen and Böttinger. Upon slow concentration of the solution of the acid lead salt, this separates in long fine needles with five molecules of water of crystallization. The copper, lead and acid lead salts show a strong tendency toward the formation of insoluble basic salts. When the solutions were concentrated on a water-bath, even at a comparatively low temperature, the basic salts separated out. This was most marked in the case of the copper salt. To obtain a good crystallization of the neutral salts it was necessary to let the water evaporate slowly in a desiccator.

A determination of the water of crystallization in the acid lead salt gave the following result:

[1] This Journal **13**, 220.

I. 0.2582 gram acid Pb salt heated to constant weight at 160°, lost 0.0333 gram.

| | Calculated for $(C_7H_4ClSO_5)_2Pb+5H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 11.72 | 11.67 |

*Barium Salt.*—The barium salt is remarkably dimorphous. It crystallizes in two forms, a compact tabular form and a yielding, spongy, arborescent form, both containing three molecules of water of crystallization, and under the same conditions losing it equally. The appearance of the spongy form when dried between folds of filter-paper is best described by comparing it with the ordinary sea-fern. The compact tabular form is the one which was most commonly obtained. Both forms sometimes occurred together in the same solution, and by redissolving one the other could be made to crystallize out under the proper conditions. The conditions for the arborescent form were found to be slow crystallization from a saturated solution at a low temperature. It was usually obtained by allowing a solution saturated at about 18° to stand over night during the winter months when the temperature of the laboratory would fall to about 5°. It was sometimes formed by exposing a beaker containing a saturated solution to the influence of the lower temperature out of doors, care being taken to prevent a too sudden chilling of the solution. The arborescent form dissolves readily in water, the tabular form even when finely powdered is much more slowly dissolved. Both forms contain three molecules of water of crystallization which are lost at 190°.

Analyses of these salts gave the following results:

I. 0.4365 gram tabular Ba salt dried at 180° to constant weight lost 0.0554 gram.

II. 0.1918 gram arborescent Ba salt dried at 190° to constant weight lost 0.0244 gram.

III. 0.4365 gram tabular Ba salt gave 0.2385 gram $BaSO_4$.

IV. 0.3128 gram tabular Ba salt gave 0.1711 gram $BaSO_4$.

| | Calculated for $C_6H_3\begin{cases}Cl\\COO\\SO_3\end{cases}>Ba+3H_2O$. | Found. | | |
|---|---|---|---|---|
| | | Tabular. | | Arborescent. |
| $H_2O$ | 12.69 | 12.68 | | 12.72 |
| Ba | 32.23 | 32.15 | 32.18 | ... |

It was at first supposed that although these dimorphous forms might have the same composition, the molecules of water of

crystallization would be combined in different ways, which would become manifest by the rate at which the water is given off. To test this supposition a portion of the tabular barium salt and of the arborescent barium salt were heated in an air-bath under the same conditions. Both portions had been powdered to the same degree of fineness. It was found, however, that the loss of water proceeded at the same rate in both forms.

*Constitution of p-chlor-m-sulpho-benzoic acid.*—As has been stated, Cöllen and Böttinger in their work on the *p*-chlor-sulpho-benzoic acid in question were unable to arrive at any conclusion concerning its constitution.

There are but two possibilities in the case of a mono-sulphonic-acid derivative of *p*-chlor-benzoic acid—the sulphonic-acid group may enter into the ortho or the meta relation, relative to the carboxyl group. Now, it has been shown in a great number of cases that, when an acid having the carboxyl and sulphonic-acid groups in the ortho relation is treated successively with phosphorus pentachloride and ammonia, the result is always an imide and not a di-amide. In the di-carboxyl acids this tendency toward an imide formation in the ortho relation is most simply illustrated in the case of phthalic acid, which by the treatment above described is converted quantitatively into phthalimide. Cases bearing more directly on a *p*-chlor-sulpho-benzoic acid are the conversion of *p*-brom-*o*-sulpho-benzoic acid into *p*-brom-sulphinide by Remsen and Bayley,[1] and the conversion of sulpho-terephthalic acid into the amide of terephthalic sulphinide by Remsen and Hall.[2]

Therefore, if the carboxyl group and the sulphonic-acid group are in the ortho relation in this *p*-chlor-sulphonic acid, the result of treating it with phosphorus pentachloride and ammonia should be *p*-chlor-benzoic sulphinide, $C_6H_3\begin{cases} CO \\ SO_2 \\ Cl \end{cases}>NH$, which has been made and studied by de Roode.[3] The substance which I obtained by treating this *p*-chlor-su pho-benzoic acid successively with phosphorus pentachloride and ammonia differs from *p*-chlor-sulphinide in all of its properties and will be shown to be a di-amide. Since *p*-chlor-benzoic sulphinide was not formed, and since the di-amide is formed, the carboxyl and sulphonic-acid groups cannot be in the ortho relation; they must be in the meta rela-

[1] This Journal **8**, 231. [2] *Ibid.* **2**, 409. [3] *Ibid.* **13**, 229.

tion, and the constitution of the acid is expressed by the formula,

$C_6H_3\begin{cases}COOH_{(1)}\\SO_3OH_{(3)}\\Cl_{(4)}.\end{cases}$ It is *p*-chlor-*m*-sulpho-benzoic acid.

*Chlorides of p-chlor-m-sulpho-benzoic acid.*—The chlorides, and the amides derived from them, were also investigated by Cöllen and Böttinger.[1] The results recorded by them seemed anomalous when compared with the reactions which sulpho-benzoic acids in general undergo when treated with phosphorus pentachloride, and a revision of the work was undertaken.

The chlorides were prepared as follows: The neutral sodium salt, dried at 160° and finely powdered, is ground together with an amount of phosphorus pentachloride equivalent to two molecules of phosphorus pentachloride to one of sodium salt. The reaction takes place spontaneously, leaving a whitish oily mass. When this is treated with water the liquid chloride separates out as a light yellow oil, which on repeated shaking with portions of water, becomes perfectly white and waxen, and on being allowed to stand under water, solidifies after a short time. The solid chloride is then freed from adhering water as well as possible by pressing between folds of filter-paper. It is then dissolved in pure anhydrous ether, in which it is very easily soluble, and is freed from a small portion of insoluble inorganic salts which are sometimes still present. If the ethereal solution is now placed in a large desiccator and the ether is allowed to evaporate slowly, needle-shaped crystals are deposited. They have the general appearance of a pure substance. On determining the melting-point, however, it is found that they begin to fuse at 35°, are semi-liquid from 70°–130°, and melt completely between 130°–155°, the range of the fusing and melting-points varying with each preparation. Recrystallization from anhydrous ether does not lead to a substance with a more satisfactory melting-point. During the process of crystallization and recrystallization in ethereal solution, fumes of hydrochloric acid were given off, which points to a decomposition of the chloride in ethereal solution. In fact, a pure chloride with a sharp melting-point, which was obtained later on by the use of another solvent, underwent change in an ethereal solution. The same chloride could be kept under water for several days without undergoing any very marked change. The use of more

[1] Ber. d. chem. Ges. **9**, 1250.

than the equivalent of two molecules of phosphorus pentachloride, and heating to 150°, leads to a compound with a tendency to become semi-liquid at a low temperature. When phosphorus pentachloride is used in the proportion of one molecule and the operation carried on at as low a temperature as possible, a compound with a tendency to become semi-liquid at a higher temperature is formed; but these variations in conditions and amount of phosphorus pentachloride did not yield a pure product.

The crystallized compound melting from 35°–155° is evidently a mixture of chlorides. Its properties agree with those of the mixture obtained by Cöllen and Böttinger, and which they supposed to be a mixture of two monochlorides:

$$C_6H_3\begin{cases}Cl\\SO_2Cl\\COOH\end{cases} \text{ and } C_6H_3\begin{cases}Cl\\SO_2OH.\\COCl\end{cases}$$

It is in the first place highly improbable that under the same conditions the carboxyl group would be acted on in one molecule and the sulphonic-acid group in another. Furthermore, the chief product of the reaction of ammonia on this mixture is a di-amide $C_6H_3\begin{cases}Cl\\SO_2NH_2,\\CONH_2\end{cases}$ which shows the preponderance of the di-chloride $C_6H_3\begin{cases}Cl\\SO_2Cl,\\COCl\end{cases}$ in the mixture. And it was found possible to separate from the mixture of chlorides two distinct chlorides, the one being the di-chloride $C_6H_3\begin{cases}Cl\\SO_2Cl,\\COCl\end{cases}$ and the other the mono-chloride $C_6H_3\begin{cases}Cl\\SO_2OH.\\COCl\end{cases}$ This was accomplished as follows:

After the chlorides have been dissolved in ether to rid them of inorganic impurities, the ethereal solution is rapidly evaporated to dryness by blowing over it a stream of dry air. In this way small portions of water which were enclosed in the chlorides before dissolving them in ether are gotten rid of. The dry chlorides are then shaken with successive portions of cold anhydrous ligroïn (70°–80°), in which the di-chloride is rather soluble and the mono-chloride insoluble. The solution of the di-chloride is concentrated by evaporation in the water-bath, care being taken to avoid the contact of water-vapor by placing over the beaker a

watch-crystal which just covers the mouth. From the concentrated solution, when cooled slowly, the di-chloride separates in flakes which are nearly pure, and by a recrystallization from ligroïn are rendered perfectly pure.

*Di-chloride of p-chlor-m sulpho-benzoic acid.*—This chloride crystallizes from ligroïn in flakes melting sharply at 42°–43°. From ether it crystallized in needles. In ethereal solution it slowly undergoes change, as is shown by a lowering and indefiniteness of its melting-point. It can be kept under cold water for a considerable length of time without decomposition. In water at a temperature above its melting-point it undergoes rapid decomposition with the formation of *p*-chlor-*m*-sulpho-benzoic acid. Treated with ammonia it is converted into the corresponding di-amide.

A determination of the chlorine was made by boiling the chloride with water containing a little nitric acid in a balloon-flask with upright condenser. After boiling for a short time the insoluble chloride is completely decomposed into *p*-chlor-*m*-sulpho-benzoic acid and hydrochloric acid. The hydrochloric acid is then precipitated as silver chloride. An analysis gave the result:

I. 0.3492 gram chloride gave 0.3625 gram AgCl = 0.0897 gram Cl.

| | Calculated for $C_6H_3\{^{Cl}_{CO\,Cl}_{SO_2Cl}$. | Found. |
|---|---|---|
| Cl, replaceable by OH | 25.93 | 25.68 |

*Mono-chloride of p-chlor-m-sulpho-benzoic acid.*—This chloride is formed in small quantity together with the di-chloride when the sodium salt of *p*-chlor-*m*-sulpho-benzoic acid is treated with phosphorus pentachloride. It remains undissolved when a mixture of the chloride is treated with cold ligroïn. It crystallizes from ether in needles. It has not yet been obtained in perfectly pure condition, as is evident from analyses and from the melting-point, which varies between 163° and 167°. Treated with ammonia, it yields a very little of the di-amide and a soluble salt. The presence of the di-amide is accounted for by the impurity of the mono-chloride hitherto obtained, which contains a little of the di-chloride. The soluble salt formed has not yet been isolated in pure condition for study. It is in all probability the corresponding amide ammonium salt.

Determinations of the replaceable chlorine in the mono-chloride were made, as in the case of the di-chloride, by boiling with water. Results were obtained as follows:

I. 0.3142 gram chloride gave 0.1799 gram AgCl = 0.0445 gram Cl.

II. 0.1820 gram chloride gave 0.1003 gram AgCl.

| | Calculated for $C_6H_3\begin{cases}SO_2OH\\COCl.\end{cases}$ | Found. I. | Found. II. |
|---|---|---|---|
| Cl, replaceable by OH | 13.91 | 14.20 | 14.27 |

A determination of the chlorine replaced by the action of ammonia was also made. For this purpose a known weight of chloride is boiled with ammonia in a balloon-flask. After acidifying with nitric acid the chlorine is precipitated as chloride. This determination of the replaceable chlorine resulted as follows:

0.3086 gram chloride gave 0.1792 gram AgCl = 0.0443 gram Cl.

| | Calcu ated for $C_6H_3\begin{cases}Cl\\SO_2OH\\COCl.\end{cases}$ | Found. |
|---|---|---|
| Cl, replaceable by $NH_2$ | 13.91 | 14.36 |

In the above analyses the amount of replaceable chlorine found is too high for the mono-chloride. It is evident that the mono-chloride melting at 163°–167° still contains a little of the di-chloride.

*Di-amide of p-chlor-m-sulpho-benzoic acid.*—By treating the mixture of the chlorides, or the di-chloride of *p*-chlor-*m*-sulpho-benzoic acid with ammonium hydroxide the di-amide is formed. This is soluble in the excess of ammonia used. For the recovery of the di-amide, the solution was evaporated until most of the free ammonia had been given off, and upon acidifying with hydrochloric acid the di-amide is precipitated. By washing with cold water the soluble salts were dissolved. The di-amide is readily soluble in hot water, and after two recrystallizations separates in excellent needle-shaped crystals which melt at 233°. This di-amide has been described by Cöllen and Böttinger as an amide-ammonium salt derived from what they supposed to be a mixture of mono-chlorides. It has been shown that this mixture is one consisting mainly of the di-chloride which, as would be expected, yields the di-amide. The di-amide resulting from the mixture of chlorides is far more insoluble than would be expected for an

ammonium salt, and does not give off ammonia by treatment with cold caustic soda. The analyses point most clearly to the di-amide.

I. 0.2791 gram di-amide by absolute method gave 28.0 cc. N at 18° = 0.03294 gram N.

II. 0.3126 gram di-amide by Liebig's method gave 0.3094 gram $BaSO_4$.

III. 0.1923 gram di-amide by Liebig's method gave 0.1914 gram $BaSO_4$.

| | Calculated for $C_6H_3\begin{cases}Cl\\SO_2NH_2\\CONH_2\end{cases}$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| N | 11.97 | 11.91 | |
| S | 13.66 | 13.60 | 13.68 |

*Amide-ammonium salt and di-anilide.*—By treating the monochloride which melts at 163°–167° with ammonia, an amide-ammonium salt is formed which probably has the constitution

$$C_6H_3\begin{cases}CONH_2\\SO_2ONH_4\\Cl.\end{cases}$$

It is much more soluble than the di-amide. It has not yet been obtained in pure condition.

The *di-anilide* formed by treating the di-chloride with aniline was obtained in pure needle-shaped crystals which melt at 219°–220°.

It is the intention of the author to pursue this investigation farther, and to reinvestigate the work done on *p*-brom-sulpho-benzoic acid, in regard to which statements analogous to those on *p*-chlor-sulpho-benzoic acid have been recorded.

This investigation was undertaken at the suggestion of Professor Remsen and carried out under his supervision, and I desire here to acknowledge my indebtedness to him.

Contributions from the Chemical Laboratory of the Case School of Applied Science.[1]

## IV.—ON THE DETERMINATION OF SULPHUR IN VOLATILE ORGANIC COMPOUNDS.[2]

By Charles F. Mabery.

The great quantity of products introduced into the petroleum industry from the fields in Ohio and Canada yielding the sulphur oils has involved many sulphur determinations, and the necessity of a rapid method capable of affording results of extreme accuracy, especially in oils containing a small fraction of one per cent. of sulphur. Several of the older methods leave nothing to be desired in point of accuracy, but they are not sufficiently expeditious for service in manufacturing operations, or in investigations which depend upon immediate information concerning the percentage of sulphur.

The first attempt to determine sulphur in organic compounds by combustion in oxygen was made by C. M. Warren,[3] the sulphuric acid formed being absorbed within the combustion-tube in plumbic peroxide. The oxides and acids formed by combustion were first distilled and collected in bromine-water as an oxidizing agent, by Sauer,[4] and this method was still further improved by Mixter,[5] who avoided the use of a rubber cork in the forward end of the combustion-tube, carried forward the volatilized substance by a current of carbonic dioxide, and suggested more efficient means for oxidation by bromine and absorption. All these methods depend upon the formation of sulphuric acid and precipitation as baric sulphate, which involves considerable labor when a large number of determinations are necessary in a limited time. To overcome this difficulty Burton[6] suggested a modification of the method of Sauer, which consists in absorbing the oxidized sulphur in a standard solution of potassic hydrate and titrating the excess of alkali with standard sulphuric acid.

Besides these methods the only other suitable means for the determination of sulphur in oils with large percentages of sulphur

[1] Proceedings of the American Academy of Arts and Sciences. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

[2] This paper is one of the series on the composition of the sulphur-petroleums.

[3] Proc. Am. Acad. **6**, 472.

[4] Ztsch. anal. Chem. **12**, 32.

[5] This Journal **2**, 396.

[6] *Ibid.* **11**, 72.

is the well known method of Carius, in which the substance is oxidized in a closed tube by means of fuming nitric acid. In its applicability to all classes of compounds, and in the accuracy of results of which it is capable, this method leaves little to be desired except perhaps in the analysis of oils containing less than 0.01 per cent. of sulphur. On account of the limited weight of substance that can be oxidized in a Carius tube another method must be selected for substances containing less sulphur. Our experience has shown that the Carius method may be relied upon in sulphur determinations to yield concordant results within a few hundredths of one per cent. Oxidation of the less volatile oils containing a small percentage of sulphur, without doubt, may be accurately accomplished in an open vessel, but with larger amounts of sulphur the action of nitric acid is so violent that it must entail loss by volatilization, unless indeed the sulphur oil is considerably diluted by a sulphur-free oil, in which case the solvent must be completely oxidized.

The great number of sulphur determinations in crude oils and products obtained from them, connected with the extended examinations which have occupied my attention during several years past, has demanded a careful comparison of the various methods as to their efficiency and economy of time. Particular attention has been given to details of the Carius method, with the precautions necessary in its successful application to the analysis of sulphur oils. The first requisite is a furnace of suitable construction to maintain an equal temperature, easily controlled in all the tubes within the furnace, without a great loss of heat by radiation. For this purpose and for Carius analyses in general I have recently had a furnace constructed which differs in certain features from any other I have seen, and it shows such a high degree of efficiency that a brief description may not be entirely devoid of interest. The body is of the ordinary cylindrical form, 75 cm. long and 25 cm. in diameter, of heavy sheet iron, and it is surrounded by two outer jackets of sheet iron each enclosing a half-inch space, and extending beneath on either side to within 6 cm. of the heating tube; it is supported upon legs of strap-iron $\frac{3}{16}$-inch thick and 2 inches wide, each entirely encircling the body at either end, for rigidity. These two air-spaces retain the heat so effectually that the hand may be borne on the outside of the furnace when the thermometer within indicates a temperature of

200°. The iron tubes are as usual of gas-pipe, with threads at either end, with caps easily movable by the fingers. With a small hole in each cap for the escape of gas, these tubes retain all glass in the most violent explosions. When several tubes are in the furnace at the same time a record of them may conveniently be kept by suspending metal tags numbered consecutively, from the holes in the caps by means of bent wire.

Fig. 1 shows the arrangement of the outer air-spaces with the position of the heating-tube. The furnace is heated by means of a gas-stove heater 45 cm. in length, with thirty-two gas-jets that will burn continuously with a flame 2 mm. high, giving a temperature within the furnace of less than 60°; by interposing an asbestos or an iron plate a considerably lower temperature may be maintained. The heating-tube is supported on two iron straps bolted to the legs, one at either end of the furnace; by means of it the heat is very equally distributed with little waste, and the glass tubes being thus evenly heated there is less danger of loss by explosion. A temperature of 200° may be obtained within twenty-five minutes after lighting the jets, and it may be maintained with jets fifteen millimeters in height, requiring a small consumption of gas; the hand may be held without discomfort for some time directly beneath the heater. The variation in temperature at different heights within the furnace is small; with the thermometer at 275° at the level of the upper tubes, the temperature at the level of the lower tubes is about 9° higher. For temperatures higher than 275° a second heating-tube is necessary.

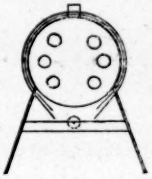


FIG. 1.

It is frequently convenient to be able to regulate within close limits the flow of gas for the required temperature without further attention after lighting the jets. The device shown in Fig. 2, which suggested itself for this purpose, consists in attaching to the end of the gas-valve by means of a screw-thread a brass cap with an index of stout copper wire moving in front of a graduated circle with a radius of about six inches.[1]

[1] Evidently this attachment has no reference to variations in temperature caused by changes in pressure on the gas within the mains. For regulating the temperature within closer limits, a gas-regulator can be inserted.

With glass tubes of large size—those we use are 15 mm. inside diameter—well sealed, and with strict adherence to certain conditions which have elsewhere been described by A. W. Smith and me,[1] there is little danger of an explosion. The quantity of nitric acid should not be in excess of twenty times the weight of the substance taken, and after heating to 175° for fifteen hours the tubes are opened—best without removing from the furnace—resealed and heated again to 250° during five to ten hours. The serious objection to the Carius method for sulphur is the slow process of oxidation, and it seems hardly possible to hasten the operation by raising the temperature, since glass tubes will not stand the great pressure.

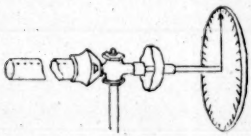


FIG. 2.

In studying various methods depending upon the oxidation of sulphur by combustion I have found that nothing less than complete oxidation gives reliable results. Many experiments on fractional combustion have shown clearly that compounds with high percentages of sulphur do not yield concordant results, even when the sulphur compound is diluted with a sulphur-free oil. I have found Burton's adaptation of the Sauer method reliable and expeditious, and with certain modifications presently to be described it is perfectly satisfactory for the analysis of oils of high as well as low percentages of sulphur. In Fig. 3 the inlet tube for oxygen or air is shown as entering through the rear stopper, as proposed by Mixter, and extending just to the centre of the constriction. In the combustion of some of the oils which we have under examination, the temperature must be maintained as high as the most infusible Bohemian glass will stand, and at such temperatures the smaller tube within is distorted if it is placed in the forward portion of the combustion-tube in the zone of greatest heat; if it terminates at the narrowest point of the constriction, continuous combustion is insured by thorough admixture of the volatilized substance with oxygen. Complete oxidation is still more certain in rapid combustion if that portion of the tube in front of the narrower part is left somewhat longer than is preferred by Sauer, Mixter, or Burton. The tubing we have in use is some-

[1] This Journal **16**, 83.

what thicker in the wall than that in ordinary use, and larger, with an inside diameter of 18 mm. It is important that the oxidation proceed as rapidly as is consistent with complete absorption, and we find that this is best accomplished in a large U-tube partly filled with broken glass. Our U-tube is 34 cm. in height, 25 mm. inside diameter, and with 50 cc. of the absorbent solution a rapid gaseous stream may be passed through without danger of loss. For low sulphur oils we use a solution of sodic hydrate of such a strength that 1 cc. equals 0.0010 gram of sulphur, and for

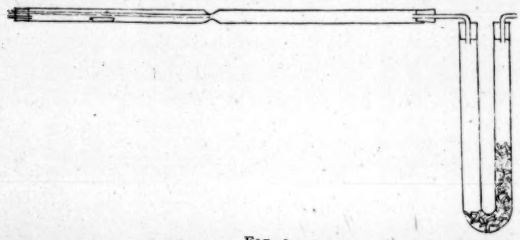


FIG. 3.

higher percentages a solution in which 1 cc. equals 0.0050 gram. Methyl-orange has been used as an indicator in all our determinations; the change in color in titrating an alkaline solution with this indicator is well defined and exceedingly delicate. The titrations may be made in the U-tube without transferring the solution after washing in the acid from the combustion-tube. To carry forward the volatilized substance it is advantageous to introduce a slow current of carbonic dioxide, as proposed by Mixter, and we have sometimes used a combustion-tube closed with a rubber cork in front and sometimes a bent tube. With substances containing a high percentage of sulphur it is doubtless safer, as Mixter suggests, to avoid the use of a cork in front.

On account of the large consumption of oxygen in burning rapidly a considerable weight of oil—at least three times the quantity theoretically required for oxidation—and finding that the combustion proceeds with equal facility in air, nearly all our determinations have been made in a current of air supplied under pressure, with the same means for exhaustion that Burton found advantageous. The operation requires close attention and 0.5 to 1 gram

of oil may easily be burned in forty-five minutes to one hour, depending upon the nature of the substance, the heavier oils especially if containing much sulphur being the most difficult to burn. The higher sulphides will not support a continuous flame, and dependence must be placed upon a very hot tube; with the more volatile oils it is sometimes difficult to maintain a continuous flame even in oxygen, the combustion proceeding in long intermittent non-luminous flashes. If the flame becomes luminous the rapidity of volatilization must be instantly checked, and the flow of air increased. The appearance of white fumes in the forward part of the combustion-tube or the absorption-tube, indicating improper adjustment as to the temperature, flow of gas, or rate of volatilization, is invariably attended with low results. The completeness of the absorption in the U-tube was tested by placing a second tube beyond it containing a similar solution, but no trace of acid was found in the second tube when the excess of alkaline hydrate in the first at the end of the analysis was not less than 15–20 cc. With a smaller excess in rapid combustions there is danger of loss. The oil for analysis is weighed in a bulb or tube of hard glass, and it is sometimes convenient to transfer most of it to a platinum or a porcelain boat, which may easily be accomplished without loss within the combustion-tube provided there is a gentle current of air inward and the combustion-tube in front has previously been heated to the required temperature.

In the examination of Ohio and Canadian sulphur petroleums for identification of the paraffin, aromatic, and unsaturated hydrocarbons, sulphur compounds, and other constituents, with which I am at present engaged, numerous determinations of sulphur have been necessary, and the extreme convenience of combustion in air has greatly facilitated the separation of the various products. As an evidence of the reliability of this method, the following results are selected, with parallel determinations by the Carius method:

| | Percentage of Sulphur. | |
|---|---|---|
| | Combustion in Air. | Carius. |
| Distillate from crude Canada oil collected at 89°–91° after one distillation under 50 mm. and seven under atmospheric pressure.... | 0.044 | 0.043 |
| Distillate from crude Ohio oil collected at 127°–129° after one distillation under 50 mm. and seven under atmospheric pressure .... | 0.0343 | 0.036 |
| Distillate from crude Canada oil collected at 115°–117° after one distillation under 50 mm. and seven under atmospheric pressure .... | 0.173 | 0.0108 |

| | | | | |
|---|---|---|---|---|
| Distillate from crude Canada oil collected at 120°–130° after one distillation under 50 mm. and five under atmospheric pressure | 0.505 | | | |
| The same after shaking five times with alcoholic mercuric chloride | 0.07 | | | |
| The same after shaking once with alcoholic mercuric chloride with the addition of solid mercuric chloride | 0.086 | | | |
| | I. | II. | | |
| Sulphur oil from Canada sludge acid | 6.3 | 6.3 | 6.47 | |
| Sulphur oil from Canada sludge acid | 17.36 | | 17.31 | |
| | I. | II. | | |
| Sulphur oil from Canada sludge acid | 16.67 | 16.76 | | |
| Canada sulphur oil | 6.15 | | 6.01 | |
| Canada sulphur oil | 13.67 | | 13.70 | |
| Crude sulphide separated by mercuric chloride from fraction 110°–115° of sulphur oil after the fifth distillation under 50 mm | 18.85 | | | |
| A fraction of the same corresponding to pentyl sulphide, percentage of sulphur, 18.39. | I. 18.53 | II. 18.55 | III. 18.67 | |

These results were obtained by six persons working independently of one another.

The oxidation of nitrogen to any considerable extent by the use of air in the combustion of sulphur compounds is evidently excluded by the close agreement of the results it yields with corresponding determinations by the Carius method. In accordance with the suggestion of a friend, from the fact that nitrous and nitric acids are formed to a greater or less extent depending upon conditions in the ordinary forms of combustion, it seemed of interest to ascertain whether these acids were present at all in the alkaline absorbent. In testing for the formation of nitrous acid, the exceedingly delicate color reaction was applied which is produced in an acid solution of a nitrite by the addition of sulphanilic acid and naphthylamine chloride. An examination of our reagents showed that the purest commercial sodic or potassic hydrate gives an intense color, and even hydrates prepared from the metals are not free from color. Pure sulphuric acid gave no reaction, and pure sodic carbonate only a faint color. We finally obtained a solution that gave not a trace of color by dissolving metallic sodium and boiling the solution for some time with metallic aluminum. With this solution as the absorbent in a

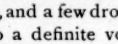
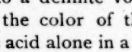
combustion of a sulphur oil, after the analysis the solution was as free from color as before when it had stood half an hour after the addition of the reagents. Since a pink color is distinctly visible in this reaction with one part of nitrogen in the form of nitrous acid in one thousand million parts of solution, it is safe to conclude that nitrous acid is not one of the products in this form of combustion.

To determine whether nitric acid is formed, after the combustion a portion of the sodic hydrate solution was neutralized, mixed with ferrous sulphate, and concentrated sulphuric acid poured beneath the solution. No color was visible at the junction of the two liquids. In a second test another portion of the alkaline solution was nearly neutralized with sulphuric acid, evaporated to dryness, and a few drops of phenolsulphuric acid added. Upon diluting to a definite volume, no difference could be perceived between the color of this solution and that given by phenolsulphuric acid alone in a blank experiment. In the combustion of sulphur oils in air, therefore, the atmospheric nitrogen is not affected.

For efficient aid in studying the details of these methods of analysis, I should acknowledge my obligations to Mr. W. O. Quayle, and to my assistants, Messrs. D. B. Cleveland and G. M. Little.

## REVIEWS AND REPORTS.

### Recent Progress in Physical Chemistry.

*Die Geschwindigkeit des Ueberganges von Aldoximen in Säurenitrile. A. Hantsch: Ztschr. phys. Chem.* **13**, 509 (1894).—The antialdoximes  differ from the stereoisomeric synaldoximes  in that only the latter, in the form of their acetates, are decomposed by the alkaline carbonates into nitriles

and acetic acid. The readiness of this nitrile formation depends to a high degree upon the nature of the substituent R, and in the effort to obtain a numerical expression for this dependence the characteristic constant of the reaction-velocity was determined for a dozen different acetates. When the process is considered to be

$$RH:C:N.OCOCH_3 = R.C:N + CH_3COOH$$

it is monomolecular and its velocity must remain proportional to the concentration of the undecomposed acetate, *i. e.*,

$$\frac{dx}{dt} = C.(A-x) \text{ or } \frac{1}{t} \log [A/(A-x)] = C,$$

when $x$ parts of the initial quantity $A$ are decomposed at the time $t$. The velocity constant $C$ furnishes a sensitive test for the purity of the aldoximes used. The compounds investigated fall into the following order with respect to readiness of decomposition:

| | | |
|---|---|---|
| 1. | Metanitro-derivative | $C = 0.000128$ |
| 2. | Parachlor " | 371 |
| 3. | Thiophene " | 408 |
| 4. | Anis " | 410 |
| 5. | Piperonal " | 474 |
| 6. | *p*-Methyl " | 475 |
| 7. | Benzaldehyde " | 552 |
| 8. | *p*-Ethoxyl " | 564 |
| 9. | *p*-Brom " | 619 |
| 10. | *p*-Iodo " | 696 |
| 11. | *p*-Cyan " | 8(?) |
| 12. | *p*-Nitro " | 8 |

These results seem to indicate no simple relation between constitution and stability.

*Ueber die Bestimmung kleiner Dissociationsspannungen, speziell krystallwasserhaltiger Salze. C. E. Linebarger: Ztschr. phys. Chem.* **13**, 500 (1894).—When two phases of a heterogeneous system are in equilibrium with a third they are also in equilibrium with each other. From this principle the conclusion has been drawn by Nernst that the dissociation-pressures of a substance whose volatile dissociation-products are soluble in some liquid are identical with the partial pressures of these products above the saturated solution of the substance (itself insoluble), and can hence be found from the solubilities of these products and their solubility-coefficients. This is tested in the present paper for various hydrated salts in equilibrium with ether at the boiling-point, the solubility of the dissociated water being calculated in each case from the boiling-point of the solution. For crystallized salts of copper, strontium, magnesium and zinc values were obtained in close agreement with the direct determinations of Frowein. It was shown also that such determinations can be

consecutively made in a given mass of ether if the salts employed be added in the order of their dissociation-pressures. The paper is an interesting contribution to the literature of Chemical Statics.

*Beiträge zur Molekulargewichtsbestimmung an "festen Lösungen."* *F. W. Küster: Ztschr. phys. Chem.* **13**, 445 (1894).—The chemical equilibrium established between caoutchouc, ether and water is an especially interesting instance of an equilibrium in heterogeneous systems involving a solid solution, for pure caoutchouc dissolves ether readily, and in the system mentioned the ether is subjected to a distribution between the solid and liquid phases. To given amounts of water and ether varying quantities of caoutchouc were added and the concentrations of the aqueous solution determined from its freezing-point. The concentration $C$ in the caoutchouc is strictly proportional to the square of that $c$ in the water; therefore, according to the law of the reaction-isotherm, the ether is bimolecular in the caoutchouc and the distribution between the two phases (at 0° C.) takes place according to the scheme

$$\underset{\text{in caoutchouc}}{(C_4H_{10}O)_2} \gtrless \underset{\text{in water}}{2C_4H_{10}O}$$

and the equilibrium constant is given by the equation

$$K \cdot C = c^2.$$

The equilibrium at higher temperatures, near 17° R., is of a yet more interesting character, for here the ratio of distribution $K$, although at first constant, increases with falling concentration. This indicates a progressive dissociation of the bimolecular ether in the caoutchouc. The ratio of the *total* concentrations approaches with falling concentration the limit 2.8, which is therefore the ratio of distribution of the monomolecular substance. The product of this ratio into the concentration of the (always monomolecular) ether in water yields then the concentration $c'$ of the monomolecular ether in the caoutchouc for each case, and this taken from the total concentration in the solid phase leaves that $C'$ of the undissociated bimolecular ether there. The dissociation-isotherm requires now the relation

$$K \cdot C' = c'^2 \quad \text{or} \quad \frac{c'}{\sqrt{C'}} = const.$$

This is the first instance of a quantitative application of the theory of dissociation to a substance dissolved in solid solution, and it is at the same time a beautiful application of Nernst's Principle of Distribution.

A continuation of the work at 0° C., whereby the concentrations were varied within very wide limits, yielded a quantitative result of the same character as that just cited; and it was found that the dissociation of the bimolecular ether in the solid solution is, at ordinary temperatures, for a given total concentration, about three times as great as at zero.

*Ueber die Dissociation von Kaliumtrijodid in wässriger Lösung. A. A. Jakovkin: Ztschr. phys. Chem.* **13**, 539 (1894).—When iodine is dissolved in aqueous potassium iodide it is supposed that a compound of the two substances is formed in the solution. If this be true, one must expect an equilibrium of the form

$$KI \,.\, mI_2 \gtrless KI + mI_2$$

to be established between this compound and its dissociation-products. In the experimental work cited, aqueous solutions containing the two substances in varying relative concentrations were shaken up with carbon disulphide at 20°, whereby any free iodine present must be distributed between the liquids in the ratio 1 : 410 (Berthelot and Jungfleisch). The degree of dissociation is then given by the ratio of the iodine-concentration in the disulphide to 410 times that of the total iodine in the iodide solution. When $a$ g-mols of potassium iodide are present per one of iodine, $x$ of which are free and $1-x$ combined, in the volume $v$ of this solution, the dissociation isotherm becomes

$$K.\frac{1-x}{v} = \frac{a-(1-x)}{v}\cdot\left(\frac{x}{v}\right)^m,$$

or

$$\frac{(a-1+x)\,x}{(1-x)\,v} = K,$$

on the assumption that $m=1$, *i. e.* that the compound $KI_3$ is formed. $K$ was found in three series of experiments to remain very constant, the tri-iodide is therefore formed and the dissociation equilibrium in the solution is

$$KI_3 \gtrless KI + I_2.$$

*Dielektrizitätskonstante und chemisches Gleichgewicht. Ztschr. phys. Chem.* **13**, 531 (1894). *Methode zur Bestimmung von Dielektrizitätskonstanten. W. Nernst: Göttinger Nachrichten* **1893**, 762.—The electrical energy of a system of charged conductors, $\frac{1}{2}\Sigma e\,V$, in which $e$ and $v$ represent quantity and potential respectively, falls to $\frac{1}{2D}\Sigma e\,V$ when the system is immersed in a medium whose specific inductive capacity is $D$. The conductors are therefore more readily separable in a medium with a high than in one with a low specific inductive capacity, and transfer from one medium to another is accompanied by a force tending to draw the system into the one with the greater $D$.

[This is perhaps more readily seen when we say that two charged and separated conductors exert upon each other an attraction which is dependent upon their charges and their distance apart, the energy of attraction being proportional directly to the two electrical quantities $\varepsilon_1$ and $\varepsilon_2$ and inversely to the distance $r$ (Coulomb). Writing $f$ for the attractive force,

$$fr = -\frac{1}{D}\cdot\frac{\varepsilon_1\varepsilon_2}{r},$$

the negative sign indicating positive attraction when the electrical quantities are of opposite sign. When the charged bodies are separated in air the proportionality-factor $D = 1$, in other media (dielectrics) the attractive energy falls to $\frac{1}{D}$ of its value in air, $D$ thus defined being the Dielectric Constant or Specific Inductive Capacity. The attractive energy between the bodies is then inversely proportional to the dielectric constant of the surrounding medium.]

Now, since the charged ions of an electrolyte must be regarded as existing independently, *i. e.*, in a certain sense separated, they must accordingly be expected to dissociate (electrolytically) more readily in media with high dielectric constants than in such with low $D$. And this is exactly what is observed, for, *e. g.*, the electrical conductivity (which, being proportional to the ion-concentration, roughly measures the dissociation) of $\frac{1}{8}$-normal hydrochloric acid in various solvents varies as follows:

| Medium. | Approximate Conductivity. | $D$. |
|---|---|---|
| Gases | 0.000000000 | 1.00 |
| Benzene | 0.0000005 | 2.26 |
| Xylene | 0.0000008 | 2.34 |
| Ether | 0.000004 | 4.06 |
| Isoamyl alcohol | 1.6 | 16.7 |
| Isobutyl alcohol | 3.1 | 18.7 |
| Ethyl alcohol | 16.0 | 25.7 |
| Methyl alcohol | 94.0 | 35.3 |
| Water | 310.0 | 79.3 |

This accounts for the depression of the conductivity of an aqueous solution on the addition of alcohol, etc. The discovery is a remarkable one, and must have an important bearing upon the further study of chemical equilibrium.

Many bimolecular substances, *e. g.*, fatty acids, dissociate primarily into monomolecular substance, and then into ions. That these two processes are related is to be anticipated, and this appears from Nernst's discovery that acetic acid is subjected to a considerably greater dissociation,

$$(CH_3COOH)_2 \gtrless 2CH_3COOH,$$

in its solution in benzene ($D = 2.3$) than when in vapor (*i. e.* in vacuum, $D = 1.0$) of the same concentration and temperature.

[This is even better illustrated by data taken by the writer from Beckmann's work on the boiling-points of the solutions of benzoic acid. This substance is entirely bimolecular in carbon disulphide ($D = 2.6$), and its increasing dissociation,

$$(C_6H_5COOH)_2 \gtrless 2C_6H_5COOH,$$

with increasing dielectric constant of the solvent is strikingly exhibited by the rapid decrease of its "mean molecular weight," as tabulated:

$M = 122$, $(M)_2 = 244$.

| Medium. | Mean $M$. | $D$. |
|---|---|---|
| Carbon disulphide | 244 | 2.6 |
| Chloroform | 214 | 4.8 |
| Ethyl acetate | 133 | 6.7 |
| Acetic acid | 123 | 9.7 |
| Ethyl alcohol | 120 | 25.7 |
| Water | $<120$ | 79.3 |

In water, and apparently in alcohol, the electrolytic dissociation comes appreciably into play. This effect should find its most rational expression in the increase of the dissociation-constant with increasing $D$, but for this the numerical material and the mathematical theory are as yet both lacking.]

That the dielectric constant is characteristic for the chemical nature of distinctive classes of compounds is evident from the following table of approximate values:

| | | | |
|---|---|---|---|
| Gases | $D = 1.0$ | Esters | $D = 6.0$–$9.0$ |
| Hydrocarbons | 2.0–2.5 | Acetic acid | 9.7 |
| Carbon disulphide | 2.6 | Alcohol | 26.0 |
| Ether | 4.0 | Water | 79.3 |

The presumed identity of the dielectric constant with the square of the index of refraction for indefinitely long waves of radiant energy promises to be of great interest in this connection.

In the last paper cited, Nernst describes a convenient method for the experimental determination of dielectric constants.

*Ueber gesättigte Lösungen von Magnesiumchlorid und Kaliumsulfat oder von Magnesiumsulfat und Kaliumchlorid. R. Loewenherz: Ztschr. phys. Chem.* **13**, 459 (1894).—As an extension of the recent work of van der Heide,[1] the author investigates the solubility-relations of all realizable combinations of potassium chloride and magnesium sulphate in water. In addition to these two salts the system is capable of producing the double compounds schoenite and carnallite, the hexa- and heptahydrates of magnesium sulphate, as well as potassium sulphate and magnesium chloride, under the proper conditions. The paper is prefaced by a general discussion of the different systems concerned, in the light of the Phase Rule of Willard Gibbs, according to which $n-1$ of the salts must be present in solid form in order to ensure a complete saturation in solutions made up of $n$ independent components. The various solubility-curves which were experimentally determined are successfully represented as surfaces in coordinate-systems of four axes, whereby a general view of the possibilities offered by the different systems is obtained. It becomes possible, for example, to foresee from the diagrams what

[1] *Loc. cit.* **12**, 416.

salts will be crystallized out upon the isothermal evaporation of any given unsaturated solution, and in what order these salts will appear. This possibility is tested in a very considerable number of cases. The paper is concluded by a tensimeter experiment employed to confirm the simple theoretical conclusion that the vapor-pressure curves of two (complex) systems must intersect at the temperature at which a transformation of either into the other may occur.

*Ueber die dispersionsfreie Molekularrefraktion einiger organischer Verbindungen. Hans Jahn und Guido Möller: Ztschr. phys. Chem.* **13**, 385 (1894).—This work is essentially a continuation of that of Landolt and Jahn[1] upon the molecular refraction of hydrocarbons and alcohols, and it consists in the determination of the dielectric constants and molecular refraction of various fatty acids, substituted hydrocarbons and of a few mixtures. The molecular refraction of the mixtures was shown not to be strictly additive; the change in the dispersion-free refraction accompanying such strictly comparable chemical processes as the replacement of a hydrogen in a benzene ring by chlorine was found to remain approximately constant; and the authors emphasize the fact that in general the refractive power is a pronounced "constitutive property."

*Théorèmes généraux sur l'etat des corps en dissolution. P. Duhem: Jour. de Phys.* (3) **3**, 49 (1894).—Any purely thermodynamical principle relating to a solution or other mixture is independent of all hypotheses concerning the chemical state of the components of the mixture; the thermodynamical laws bear in this respect only upon the gross composition of the system as this is determined by analysis. One cannot expect thermodynamics therefore, when taken entirely alone, to determine what the chemical state of any given dissolved substance must be. But the thermodynamical method, when employed in connection with certain assumptions drawn from experience, makes possible a determination of this chemical state, and the results reached will possess the same degree of reliability which attaches to the experience from which the deduction is drawn. This is in reality the manner in which the theory of dissociation and the theory of solutions are treated by thermodynamical investigators at the present time. Duhem presents a rigorous proof for the above statements.

*Beiträge zur Kenntniss der photochemischen Wirkung in Lösungen. M. Roloff: Ztschr. phys. Chem.* **13**, 327 (1894).—A systematic study of two photochemical reactions, that of ammonium oxalate upon mercuric chloride, and the decomposition of oxalic acid by bromine. Both processes are found to be very

[1] *Loc. cit.* **10**, 289.

complicated, yet apparently to consist essentially in a transfer of electrical charges from one set of ions to another under the influence of light. An effort is made to bring this result into connection with the electromagnetic theory of light, according to which light is a manifestation of electrical wave-motion.

*Ueber die Hydrolyse von Salzen schwacher Säuren und schwacher Basen. S. Arrhenius: Ztschr. phys. Chem.* **13**, 407 (1894).—By means of a spectrophotometric method Lellmann and Schliemann[1] have recently studied the hydrolytic action of water upon the helianthine salts of several fatty acids, whereby these salts are partially decomposed into helianthine and free acid. In the present paper Arrhenius calculates their results, employing the Guldberg-Waage equation of equilibrium,

$$D(\text{water}) \times D(\text{salt}) = D(\text{acid}) \times D(\text{helianthine}),$$

the symbol $D$ indicating the electrolytically dissociated portions of the several electrolytes. This equation is shown to require an amount of decomposition agreeing very fairly with the observed results. Lellmann and Schliemann were accordingly not justified by these experiments in attacking the hypothesis of electrolytic dissociation.

*Löslichkeit des sauren Kaliumtartrats bei Gegenwart anderer Salze. A. A. Noyes und A. A. Clement: Ztschr. phys. Chem.* **13**, 412 (1894).—Experiments to determine the solubility of the acid potassium tartrate at 25°, both alone and in the presence of varying amounts of other potassium salts. The solubility is depressed equally by the chloride, bromide and iodide, and this depression becomes successively less when the nitrate, chlorate and sulphate are employed. The acetate increases the solubility because of the formation of much undissociated acetic acid; hydrochloric acid and various sodium salts effect an increase likewise, and for a similar reason. The results are in satisfactory accord with the ion theory.

*Die Wasserstoffabspaltung bei dem sauren Kaliumtartrat. A. A. Noyes: Ztschr. phys. Chem.* **13**, 417 (1894).—A measurement of the velocity of the inversion of cane-sugar brought about by the acid potassium tartrate at 100°, using the method employed by Trevor, shows this salt to be more strongly acid than any other which has been yet investigated, with the single exception of the acid sodium oxalate. A calculation of the ion-equilibrium in the solution indicates the presence, at this temperature, of some eighteen per cent. free undissociated tartaric acid and fifty-three per cent. of the univalent anion produced by the primary dissociation.

[1] Lieb. Ann. **274**, 160.

*Ueber die Wärmeausdehnung einiger Lösungen in Alkohol, Aether, Benzol und Schwefelkohlenstoff. G. Tammann und W. Hirschberg: Ztschr. phys. Chem.* **13**, 543 (1894).—From the theorem maintained by Tammann that solutions behave in many respects as though consisting of pure solvent under high pressures, and the fact that water differs from all other liquids in that its coefficient of expansion $\frac{dv}{dT}$ is greater under high pressures than under low ones, it is concluded that aqueous solutions must expand with rising temperature more rapidly than pure water does, the rate increasing with rising concentration, and that solutions in other solvents must exhibit the opposite behavior. The latter part of this proposition is tested in the present paper. Experiments with solutions of various substances in alcohol and ether seem to show in fact that the curves of the specific volumes as temperature-functions under constant pressure do tend to coincide with the curves for the solvents if the pressure in each case be considered to be increased a certain amount.

*Ueber die Affinitätsgrössen einiger schwefelhaltiger Substitutionsderivate von der Essigsäure und der Propionsäure. J. M. Lovén: Ztschr. phys. Chem.* **13**, 550 (1894).—The dissociation-constants of a number of organic acids containing sulphur were determined from the electrical conductivities of their aqueous solutions. The substitution of $SO_2$ was observed in every case to produce a stronger acid than does the introduction of sulphur alone.

*Ueber die Verseifungsgeschwindigkeit einiger Ester. A. de Hemptinne: Ztschr. phys. Chem.* **13**, 561 (1894).—In order to supplement the work of Reicher upon the relative velocities with which various esters are saponified by bases, the author has undertaken a determination of the corresponding velocities when the action is brought about by acids. The reactions are monomolecular; it was found that the velocities for the methyl and ethyl esters or the ethyl and propyl esters of given acids are always in a constant ratio, and that the same is true for the acetates and propionates or the propionates and butyrates. That is to say, from the velocities of saponification of a series of acetates the velocities for the corresponding esters of any other acid are calculable when that for one of them is known. This holds also for the saponification by bases. The nature of the component alcohol is found to have a greater influence in determining the velocity than has that of the acid.

The catalytic effect of the hydroxyl ion in effecting saponification greatly exceeds that of the hydrogen ion, yet there is no proportionality between the two. Two gaseous systems were investigated: hydrochloric and hydriodic acid gases were observed to exert a very considerable accelerating influence upon the saponification of the vapor of ethyl acetate.

*Ueber den Einfluss der chemischen Konstitution organischer Stoffe auf ihre Fähigkeit feste Lösungen zu bilden. G. Ciamician: Zischr. phys. Chem.* **13**, 1 (1894).—The tendency of pairs of organic compounds to form mixed crystals (solid solutions) may be investigated by observing whether either one when in dilute solution in the other causes abnormally small freezing-point depressions. The study of a considerable number of pairs of aromatic compounds tends to show that this tendency depends in some definite manner upon the "constitution" of the substances and also upon their melting-points and their crystal form.

*Note on the Law of Transformation of Energy and its Applications. W. Peddie: Proc. Roy. Soc. Edinb.* **19**, 253 (1893).—The investigation of the relations subsisting among various physical quantities, and which are exemplified in the different transformations of energy, are usually treated by mathematical methods of such nature as to be unavailable to any who are unacquainted with the higher mathematics. Yet these relations may be developed in an elementary manner. When $a, b, c, \ldots$ represent the quantities which fix the condition of a system, the change of energy in a process in the system is

$$dE = \frac{\partial E}{\partial a}\,da + \frac{\partial E}{\partial b}\,db + \frac{\partial E}{\partial c}\,dc + \ldots$$

or

$$dE = A\,da + B\,db + C\,dc + \ldots$$

where $A, B, C, \ldots$ may be termed the *forces* producing the changes $da, db, dc, \ldots$ They are the quantities upon whose magnitude the tendency to change depends. If the system return to its original state,

$$A\,da + B\,db + C\,dc + \ldots = 0,$$

an equation expressing the law of conservation. When only two forms of energy come into question we have, reckoning energy added as positive,

$$d.A\,da - d.B\,db = 0.$$

This relation is employed to derive the four "thermodynamical relations," the "vaporization-formula" and the familiar equations representing the equilibrium-relations between

Heat and Electrical Energy,
Electrical Energy and Work,
Electrification and Vapor-Pressure,
Surface-Tension and Vapor-Pressure,
Induced Electromotive Forces.

This paper was read before the Royal Society of Edinburgh within four weeks of the date of the presentation of Ostwald's entirely similar paper to the Royal Saxon Academy at Leipzig.[1]

[1] See This Journal **15**, 671.

This remarkable coincidence emphasizes the undoubted fact that the time is ripe for the systematic development of the Energy Theory.

*Elektromotorische Kräfte zwischen verschieden gekrümmten Quecksilberelektroden in einer Quecksilbersalzlösung. T. Des Coudres: Wied. Ann.* **46**, 292 (1892).—Two mercury surfaces at the same level in a solution of mercurous nitrate were maintained with different surface-tensions by pressing one against parchment paper by means of a mercury column of the height $h$; the other surface was left free. The electrical energy producible by the system must be equivalent to the work to be gained in a transfer of the mercury from the height $h$, that is to say, for an equivalent weight of 200 grams, to $200 \times 980 . h$ in absolute units. The corresponding electrical quantity is the familiar 96540 coulombs, and the desired difference of potential between the surfaces is $V$; the electrical energy is therefore $96540\,V$, and we have

$$200 \times 980 . h = 96540\,V$$

or

$$V = \frac{200 \times 980 \times h}{96540} \times 10^{-7} \text{ volts},$$

since one volt-coulomb is $10^7$ ergs. The agreement of the observations with the requirements of the theory is excellent, as may be seen from the following table:

| $h$. | $V$ theory. | $V$ observed. |
|---|---|---|
| 36 cm. | $7.2 \times 10^{-6}$ volts | $7.4 \times 10^{-6}$ |
| 113 | 23. | 21. |

*Unpolarisierbare elektrolytische Zellen unter dem Einflusse der Centrifugalkraft. T. Des Coudres: Wied. Ann.* **49**, 284 (1893).—When a glass tube containing an electrolytic solution is supported horizontally upon a disk which is rapidly rotated in a horizontal plane, the centrifugal force thereby produced tends to separate the faster ion from the one with a less velocity of migration, and to thus give rise to an electromotive force tending to restore the original uniform distribution. When platinum electrodes are inserted in the tube at given distances, $r_1$ and $r_2$, from the axis of rotation, the difference of potential $V$ between them, after a uniform velocity of rotation has been established, may be directly measured by suitable connections with a sensitive galvanometer.

When the centrifugal energy $E_c$ is in balance with the kinetic energy $E_k$ of the rotating system, the energy-equilibrium is expressed by

$$dE_c = dE_k,$$

or, since $E_k = \frac{1}{2} m v^2$ and $v = \frac{2\pi r}{t}$ (setting $r$ and $t$ for radius, and time of one revolution),

$$dE_c = m \left( \frac{2\pi}{t} \right)^2 r dr .$$

The centrifugal energy between the electrodes at $r_1$ and $r_2$ is, therefore—replacing $1/t$ by $R$, the number of revolutions per second,

$$\Delta E_c = \boldsymbol{m}\,(2\pi/t)^2 \int_{r_1}^{r_2} r\,dr$$
$$= 2\boldsymbol{m}\pi^2\,(r_2^2 - r_1^2)\,R^2.$$

This difference of centrifugal energy must be equivalent to the electrical energy which would be expended in restoring the system to its initial state, *i. e.*, equivalent to $V.1$ for each coulomb —and for each coulomb the actually redistributed mass $\boldsymbol{m}$ of the electrolyte is $\frac{u}{u+v}\,C - \frac{v}{u+v}\,A$, when $C$ and $A$ grams of cation and anion respectively migrate per coulomb, and $u$ and $v$ stand for the relative velocities of these ions. The above relation assumes then the form

$$V = 2\left(\frac{u}{u+v}\,C - \frac{v}{u+v}\,A\right)\pi^2\,(r_2^2 - r_1^2)\,R^2.10^{-7}\text{ volts},$$

the factor $10^{-7}$ converting the absolute units into volts because of the definition of a volt-coulomb as $10^7$ ergs. This theory was tested with a solution of cadmium iodide, the following very satisfactory results being obtained.

| $V$ observed. | $R$ corresponding thereto. | $R$ employed. |
|---|---|---|
| 155 microvolts | 5.2 per second. | 5.8 |
| 75.3 | 3.7 | 3.87 |
| 37.4 | 2.6 | 2.9 |

*Der zeitliche Verlauf der Selbstpolarisation in geschlossenen Amalgam-Concentrationselementen. T. Des Coudres: Wied. Ann.* **52**, 191 (1894).—The velocity of the isothermal diffusion of a dissolved substance depends upon the osmotic pressure of the substance and the frictional resistance of the solvent. The same is true of a metal, as zinc, dissolved in mercury to form an amalgam. Suppose a zinc electrode to be suspended in a zinc sulphate solution which is in contact with a mass of mercury, and a constant current to be passed up to the time $t = T$ from the zinc to the mercury. A zinc amalgam is thereby formed. Suppose, further, the mercury to be connected through an electrometer with a second zinc rod in the sulphate solution; the electrometer indicates at first the difference of potential between the poles of a cell Zn | $ZnSO_4$ | Hg, and then the rapid fall due to the electrolytic solution-pressure of the zinc in the amalgam. Since for ordinary concentrations the dissolved zinc follows the gas-laws, the observed difference of potential $E$ is given by the relation (Nernst)

$$E = \frac{0.86}{2}\,\theta \cdot \log_e \frac{v}{u} \cdot 10^{-4}\text{ volts},$$

in which $\theta$ signifies the absolute temperature, $v$ the concentration

corresponding to the electrolytic solution-pressure of the zinc, and $u$ the concentration of the amalgam. Des Coudres eliminates $v$ by considering the difference $E_{12}$ of E.M.F. between two surface-concentrations $u_1$ and $u_2$.

$$E_{12} = \frac{1.981}{2} \cdot \theta \log_{10} \frac{u_1}{u_2} \cdot 10^{-4} \text{ volts.}$$

After the time $T$ the deposited zinc diffuses from the surface into the mercury, thus causing the observed E.M.F. to gradually rise. The rate of diffusion, measuring distances $x$ normal to the surface, is (Fick)

$$\frac{\partial u}{\partial t} = k \cdot \frac{\partial^2 u}{\partial x^2}$$

($k$ = diffusion-constant), and when one sets $x = 0$ in the integral of this equation, the surface-concentration of the amalgam as a function of the time is obtained. The above expression for $E_{12}$ is thereby converted into the form

$$E_{12} = 0.029 \log_{10} \frac{\sqrt{t_1} - \sqrt{t_1 - T}}{\sqrt{t_2} - \sqrt{t_2 - T}} \text{ volts,}$$

which permits the calculation of this peculiar polarization-phenomenon in its change with the time. That the theory is in excellent accord with the observations appears from the following measurements made at 20° C.

$T = 10'$.

| $t_1$. | $t_2$. | $E_{12}$ observed. | $E_{12}$, theory. |
|---|---|---|---|
| 15′ 30″ | 20′ | 0.00232 volts | 0.00246 volts |
| 20′ | 30′ | 344 | 334 |
| 30′ | 40′ | 199 | 215 |
| 40′ | 50′ | 166 | 160 |
| 50′ | 110′ | 503 | 535 |
| | | 0.01444 | 0.01490 |

A discussion of the annoying sources of experimental error leads to a theoretical treatment of the theory of the self-polarization of a Zn|$ZnSO_4$|Hg cell as time-function. After a formidable integration of the partial differential equation concerned, which is accomplished by the aid of the Fourier-Cauchy method, a satisfactory relation between the surface-concentration and the time, and in consequence between the E. M. F. and the time, is arrived at.

J. E. Trevor.

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Die Lehre von der Elektrizität. G. Wiedemann. 2d ed. Vol. II. Large 8vo, 1126 pp. F. Vieweg & Sohn, Braunschweig, 1894. Price: in paper, 28 marks; bound, 30 marks.

The second volume of Wiedemann's great work on electricity has followed the first with a gratifying promptness, and this

volume receives a special welcome from the chemical world for the reason that it treats almost entirely of electrochemistry. The style of presentation is the historical-critical, and it is probably true that no contribution of any importance to electrochemical science, appearing before July 1893, has been omitted from the discussion. This fact makes the work extremely valuable as a book of reference, and no less so as a text-book for the electrochemical specialist. Its usefulness in the latter direction is increased by the unusually independent attitude which the author maintains towards the more recent developments of the hypothesis of free ions in electrolytic solutions. The text is carefully and clearly written and has been well printed. The book is one which no student of electrical or electrochemical matters can afford to be without.

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PHYSIKALISCH-CHEMISCHE TABELLEN. H. LANDOLT & R. BÖRNSTEIN. 2d ed. 4to, 563 pp. J. Springer, Berlin, 1894. Bound in moleskin: 24 marks.

One of the most important publications of the year in the literature of physical chemistry is the new edition of Landolt and Börnstein's tables of physical and chemical data. The amount of material included has been increased enormously over that contained in the earlier edition, and it has been rendered more valuable by the addition of citations of all the sources from which the data given are drawn. Among the features of more immediate interest to chemists and physical chemists are the tables of atomic weights, of the freezing- and boiling-points of liquids and solutions, of densities, solubilities, vapor-pressures, critical constants, specific heats, heats of fusion, of vaporization and of combustion, electrical conductivities and dielectric constants. As a book of reference for the laboratory the work is indispensable. The typographical work has been executed with great care and elegance.

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DIE WISSENSCHAFTLICHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. W. OSTWALD. 8vo, 187 pp. W. Engelmann, Leipsic, 1894. Price: in paper, 4 marks; bound, 4.50 marks.

The little book before us contains an orderly application of the new theory of solutions to the processes of ordinary chemical analysis. By throwing light upon the nature of the operations concerned it is calculated to make them mean to the student very much more than just so many mechanical manipulations. The charmingly simple manner of presenting the theory of the chemical equilibria between solutions and the precipitates formed from them, the theory of titration and of indicators, and the familiar theory of the "abnormal reactions" of certain elements, calls for especial mention. The latter half of the book is a systematic exposition of the more prominent characteristics of the different

analytical groups, treated from the point of view of the physical chemistry. The simple character of the little work is its chief merit; it should be in the hands of every student of chemistry.

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THE THEORY OF HEAT. THOMAS PRESTON. Large 8vo, 719 pp. Macmillan & Co., New York, 1894. Price $5.50.

For the reason that the thermodynamical theory of chemical equilibrium has become one of the most important chapters of theoretical chemistry, the appearance at this time of a clearly written text-book in English upon the subject of heat is to be greeted with pleasure. Preston's Theory of Heat is, in a general and descriptive way, quite a comprehensive work; it readily supplies therefore a good idea of the general concepts and laws of the subject, without the introduction of formidable difficulties of mathematical analysis. The long chapter on pure thermodynamics is of exceptional interest and value; in it a lucid account of fundamental principles is made to lead logically and easily to the theory of the thermodynamical potential, the great energy theory of chemical equilibrium and electrochemistry. As a suitable introduction to the principles upon which the thermodynamical theory of chemical processes stands, the book is to be warmly recommended.

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ELEKTROCHEMIE, IHRE GESCHICHTE UND LEHRE. W. OSTWALD. Large 8vo. Veit & Co., Leipsic, 1894. Price: 2 marks per number of 80 pages.

In this new work Ostwald has undertaken to supply an exhaustive account of the development of the science of Electrochemistry from the time of the earliest observations of electrochemical action. In the three numbers already issued the experimental researches of Galvani and Volta, the more distinctly chemical work of Ritter, and the discoveries of Davy in electrolysis, are in particular very fully treated. The historical development of the subject is rendered especially vivid by liberal quotations from the sources which are cited, and the comment upon these sources is made in a masterly way. The appearance of such a monumental work at the present time is most opportune, for the first act of the electrochemical drama may be said to have just come to a close, an entirely new epoch in the development of the subject having been inaugurated by the brilliant discoveries of Nernst. The book is to comprise some eight or ten numbers, all of which are promised for this year (1894); their issue will be impatiently awaited.

J. E. TREVOR.

CORNELL UNIVERSITY.

## JOSIAH PARSONS COOKE.

Josiah Parsons Cooke was born in Boston, Massachusetts, on October 12, 1827, and died in Newport, Rhode Island, September 3, 1894. In spite of rather a frail childhood, he entered Harvard College in 1845, was graduated with the class of 1848, and after a year in Europe was appointed tutor in mathematics at the college. Before that time there had been for many years no systematic instruction in chemistry given to undergraduates, and since Mr. Cooke's interest in the subject was well known, he was invited to give a series of chemical lectures in addition to his other work. His own knowledge of chemistry was chiefly self-taught, for naturally little was to have been gained from the disjointed lectures of his undergraduate days. During his stay in Europe he studied for some months with Regnault in Paris; but with this exception, his broad chemical knowledge was acquired by his unaided efforts.

In 1850 he was appointed instructor of chemistry and mineralogy at Harvard, and just at the close of the year was made Erving Professor, succeeding Professor Webster. After another six months in Europe he returned with apparatus and chemicals, and made an immediate attempt to establish an experimental course of instruction at Cambridge. At first his work was greatly hampered by the necessity of his giving lectures at the Harvard Medical School in Boston, but for seven years he taught qualitative and quantitative analysis to those undergraduates who cared to do the extra work. In 1858, when Boylston Hall was built, qualitative analysis was allowed to count for the bachelor's degree, and Professor Cooke was relieved of the irksome lectures at the Medical School. Ten years later he succeeded in introducing a new elective course on mineralogy; and since that time the growth of the Chemical Laboratory of Harvard College under his direction and President Eliot's administration has been continuous and rapid.

Professor Cooke's untiring zeal collected the subscriptions for the building of the new laboratory and mineral cabinet; his influence was the chief power which raised chemistry to the rank of a liberal study in Cambridge; and his energetic championship of the advantages of a scientific education has had a very far-reaching effect upon the whole educational system of America. His elementary lectures to the Freshmen were always extremely popular, and the unusual applause which greeted the Professor each day upon his appearance and his conclusion was quite sincere. Besides these lectures he gave instruction for years in physical

chemistry and chemical philosophy, and until recently in quantitative analysis as well.

In 1882 the degree of LL. D. was conferred upon Professor Cooke by the University of Cambridge, England. He was a very energetic member of the American Academy of Arts and Sciences, having been its corresponding secretary for years before his election as president, in 1892. He belonged also to the National Academy. As a popular lecturer he was unusually successful, having delivered several courses of lectures at the Lowell Institute in Boston, besides many elsewhere.

About thirty-five years ago Professor Cooke married Miss Mary Huntington, of Lowell, Massachusetts, who survives him. His summers were usually spent quietly at Newport, in his house overlooking the beach. He was, however, an appreciative traveller, and brought home many entertaining reminiscences from his occasional journeys to Europe, Egypt, and the West.

Professor Cooke is very well known as a writer. Following are the titles of his books, most of which have gone through several editions. In every case the date of the first edition is given below:

Chemical Problems and Reactions (1857).
Elements of Chemical Physics (1860).
Religion and Chemistry (1864).
Principles of Chemical Philosophy (1868).
The New Chemistry (1874).
The Credentials of Science the Warrant of Faith (1888).
Laboratory Practice (1891).

Besides these books and a number of addresses upon liberal culture and of memoirs of celebrated men, Professor Cooke wrote many monographs upon scientific subjects. The titles of these papers are given below:

The Relation between the Atomic Weights. 1854.—Mem. Am. Acad. [New Ser.] **5**; Am. J. Sci. [2] **17**, 387.

On two new Crystalline Compounds of Zinc and Antimony. 1854.—*Ibid.* [2] **18**, 229.

On a new Filtering Apparatus. 1854.—*Ibid.* [2] **18**, 127.

On the Law of Definite Proportions in the Compounds of Zinc and Antimony. 1855.—*Ibid.* [2] **20**, 222.

Crystalline Form not necessarily an indication of definite Chemical Composition. 1860.—*Ibid.* [2] **30**, 194; Phil. Mag. **19**, 405.

On the Dimorphism of Arsenic, Antimony and Zinc. 1861.—Am. J. Sci. [2] **31**, 191.

On the Spectroscope. 1862.—*Ibid.* [2] **34**, 299.

On the Cleavage of Galena. 1863.—*Ibid.* [2] **35**, 126.

An improved Spectroscope. 1863.—*Ibid.* [2] **36**, 266.

Crystallographic examination of Childrenite. 1863.—*Ibid.* [2] **36**, 257.

Crystallographic examination of the acid tartrates of Caesia and Rubidia. 1864.—*Ibid.* [2] **37**, 70.

On a Spectroscope with many prisms. 1865.—*Ibid.* [2] **40**, 305.

On the Projection of the Spectra of the Metals. 1865.—*Ibid.* [2] **40**, 243.

On the Aqueous Lines of the Solar Spectrum. 1866.—*Ibid.* [2] **41**, 17.

Separation of Iron and Alumina, etc. 1866.—*Ibid.* [2] **42**, 78.
Analysis of Danalite of Rockport. 1866.—*Ibid.* [2] **42**, 73.
On Cryophyllite. 1867.—*Ibid.* [2] **43**, 217.
On certain Lecture Experiments, etc. 1867.—*Ibid.* [2] **44**, 189.
Crystallographic examination of some American Chlorites. 1867.—*Ibid.* [2] **44**, 201.
A method of determining the Protoxyd of Iron in Silicates not soluble in the ordinary mineral acids. 1867.—*Ibid.* [2] **44**, 347.
Atomic Ratio. 1869.—*Ibid.* [2] **47**, 386.
Absolute system of Electrical Measurements. 1870.—Franklin Institute.
The Vermiculites. 1874.—Proc. Am. Acad. **9**, 35.
Melanosiderite. 1875.—*Ibid.* **10**, 451.
On two new varieties of Vermiculites (with F. Gooch). 1875.—*Ibid.* **10**, 453.
On a new mode of manipulating Hydric Sulphide. 1876.—*Ibid.* **12**, 113.
On the process of Reverse Filtering. 1876.—*Ibid.* **12**, 124.
Revision of the Atomic Weights of Antimony. 1877.—*Ibid.* **13**, 1.
Re-examination of some of the haloid compounds of Antimony. 1877.—*Ibid.* **13**, 72.
The Radiometer. 1878.—Pop. Sci. Monthly, May.
The Atomic Weight of Antimony. 1879.—Proc. Am. Acad. **15**, 251.
On Argento-antimonious Tartrate. 1880.—*Ibid.* **16**, 393.
On the Oxidation of Hydrochloric Acid Sol Antimony in the atmosphere. 1880.—Am. J. Sci. [3] **19**, 464.
On the Solubility of Chloride of Silver in water. 1881.—*Ibid.* [3] **21**, 221.
Additional Experiments on the Atomic Weight of Antimony. 1881.—Proc. Am. Acad. **17**, 1–22 (contains reprints also of a few of the preceding papers).
The Boiling-point of Iodide of Antimony, and a new form of Air Thermometer. 1881.—*Ibid.* **17**, 22.
A simple method for Correcting the Weight of a Body for the Buoyancy of the Atmosphere when the Volume is unknown. 1883.—Am. J. Sci. [3] **26**, 38.
Possible Variability of the Law of Definite proportions. 1883.—*Ibid.* [3] **26**, 310.
The relative values of the Atomic Weights of Oxygen and Hydrogen (with T. W. Richards). 1887.—Proc. Am. Acad. **23**, 149.
Additional note on the relative values of the Atomic Weights of Oxygen and Hydrogen (with T. W. Richards). 1888.—*Ibid.* **23**, 182.
The Chemical Elements. 1889.—Pop. Sci. Monthly, **34**, 733.
On a new method of determining Gas-densities. 1889.—Proc. Am. Acad. **24**, 202.

THEODORE WILLIAM RICHARDS.